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KINETICS AND CATALYSIS

КИНЕТИКА И КАТАЛИЗ/KINETIKA I KATALIZ

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KINETICS AND CATALYSIS

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CONTENTS

	PAGE ENG.	PAGE RUSS.
From the Publisher	i	
Editorial	1	3
The Structure of Molecules and Reactivity in Catalysis. A. A. Balandin	3	5
An Investigation of the Part Played by Electronic Factors in Catalysis. S. Z. Roginskii	13	15
The Main Concepts in the Electronic Theory of Catalysis on Semiconductors. F. F. Vol'kenshtein	29	32
The Use of Electron Paramagnetic Resonance in Chemistry. V. V. Voevodskii	37	45
Chain and Molecular Reactions of Intermediates in the Oxidation of n-Decane. Z. K. Maizus, I. P. Skibida, N. M. Émanuél', and V. N. Yakovleva	46	55
The Mechanism of Metallic Oxide Catalyzed Oxidations. V. A. Roiter	53	63
The Mechanism of Isotopic Exchange of Hydrogen on Platinum Films. G. K. Boreskov and A. A. Vasilevich	59	69
The Nature of the Change in Heat and Activation Energy of Adsorption with Increased Surface Coverage. N. P. Keier	74	83
The Catalytic Function of Metal Ions in a Homogeneous Medium. L. A. Nikolaev	83	94
Kinetic Method for Determination of Adsorption Coefficients. 1. Adsorption Coefficients of Water, Ether and Ethylene on Alumina. K. V. Topchieva and B. V. Romanovskii	93	106
The Development of Chemical Activity of Intermediate Forms of a Type of Surface Hydrocarbon Radicals in the Heterogeneous Catalysis of Carbon Monoxide and Olefins. Ya. T. Éidus	104	117
Liquid-Phase Contact-Catalytic Oxidation of Organic Compounds on Noble Metals. I. Oxidation of Monophenyl Ether of Ethylene Glycol to Phenoxyacetic Acid. I. I. Ioffe, Yu. T. Nikolaev, and M. S. Brodskii	112	125
Structure and Texture of Aluminum–Chromium–Potassium Catalysts and Their Activity and Selectivity in the Decomposition of i-C_3H_7OH. A. M. Rubinshtein, N. A. Pribytkova, V. A. Afanas'ev, and A. A. Slinkin	116	129
The Influence of Acidity of Oxide Catalysts on Their Catalytic Activity. I. Polymerization of Isobutene. V. A. Dzis'ko and M. S. Borisova	130	144
The Determination of Stability Conditions for Exothermic Contact Processes in a Pseudo-boiling Bed. M. G. Slin'ko	138	153
Principles of Reactor Operation Control in Large-Tonnage Catalytic Processes. D. I. Orochko and A. P. Zinov'eva	148	162
Simon Zalmanovich Roginskii (on his 60th birthday)	156	170
CURRENT EVENTS		
All-Union Conference on Organic Catalysis in Moscow. E. I. Klabunovskii	158	172

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

FROM THE PUBLISHER

Consultants Bureau is proud to present this first issue of a complete English translation of KINETICS AND CATALYSIS. This important new Soviet journal is the only authoritative periodical which specifically covers these fields, and it will provide English-speaking scientists with a comprehensive and up-to-date survey of research and development in kinetics and catalysis.

As a result of the two-year contract signed with Mezhdunarodnaya Kniga, the official Soviet book agency, in 1960, Consultants Bureau is receiving advance page proofs and original art work and photographs for this journal, thus ensuring regular publication of a very high quality. The translation will be published not more than six months after the original Russian by the end of 1961. The translation will bear volume and issue numbers identical with the Russian original. All tabular and illustrative material is reproduced integral with the English text, which is translated by bilingual scientists who are experts in these particular fields. Transliteration is by the British-American system.

The addition of KINETICS AND CATALYSIS to the Consultants Bureau program brings its total of cover-to-cover translations of Soviet scientific and technical journals to 34. More than half of these journals are produced for American learned societies. The company's twelve years of experience in the translation and publication of journals such as this one will be constantly applied toward maintaining and improving the quality of this new translation.

EDITORIAL

Translated from Kinetika i Kataliz, Vol. 1, No. 1, pp. 3-4, May-June, 1960

The May 1958 Plenary Session of the Central Committee and the Twenty-First Congress of the Communist Party of the Soviet Union adopted an extraordinary program for accelerated development of the chemical industry. It is intended that 100,000,000,000 rubles be spent during the period 1959-1965 on capital investment and other measures for the development of chemical industry.

Chemical science is confronted with great tasks in the accomplishment of this program. The most important of these tasks is the creation of scientific principles whereby chemical conversions may be controlled. Fulfillment of this task requires discovery of the laws governing the mechanism and kinetics of chemical reactions and development of methods for regulating their direction and rate by variation of the conditions and the character of catalyst action.

Catalysis is now the most common method for causing chemical conversions in industry; in many respects it determines the rate of development of the chemical industry. The possibility of obtaining new, cheap products and adoption of new raw materials in industry often depend on the discovery of suitable catalysts.

Discovery of the laws governing chemical kinetics and catalysis is important not only in the development of chemical industry, but also in power engineering, metallurgy, oil refining, and other branches of the national economy. These laws are exceptionally important in the biological sciences, where selective catalytic action of enzymes is the main method of regulation of the most important functions of living organisms.

The number of investigations concerned with the kinetics of chemical change and catalysis is very large and is growing rapidly. They will also be extended considerably in the new scientific center, the Siberian Division of the Academy of Sciences of the USSR, where the first Institute of Kinetics and Combustion and Institute of Catalysis to be established in our country are being founded, together with institutes of organic chemistry, inorganic chemistry, etc. Accordingly, it was considered appropriate to include with the new journals of the Academy of Sciences the special journal "Kinetics and Catalysis" for systematic publication and discussion of research in the fields of chemical kinetics and catalysis.

The journal will publish original theoretical and experimental papers on the kinetics of chemical change in gases, solutions, and solid phases; investigations of intermediate active particles (radicals, ions); combustion; mechanism of homogeneous and heterogeneous catalysis; scientific principles of catalyst selection; investigations of catalyst structure; catalytic processes of practical importance; influence of mass and heat transfer on the kinetics of chemical change; methods for calculating the design of chemical reactors, and scale-up methods.

Serious attention will be devoted to methods for investigating the mechanism and kinetics of chemical reactions, and catalyst properties and structure.

Letters to the editor, dealing with the results of investigations which are of special significance, will be given priority in publication.

The journal will also publish surveys summarizing recent advances in important problems of catalysis and kinetics of chemical change, discussion articles, bibliographical information, and reports of conferences and meetings.

In addition to work carried out in the Soviet Union, papers by leading foreign scientists will be published in the journal.

The Editorial Board hopes that publication of the journal will facilitate and improve the supply of information to numerous scientists and engineers about the work being done in the field of chemical kinetics and catalysis, will speed up the practical applications of this work, and will stimulate fruitful discussion of the most important problems in the kinetics of chemical change.

THE STRUCTURE OF MOLECULES AND REACTIVITY IN CATALYSIS*

A. A. Balandin

N. D. Zelinskii Institute of Organic Chemistry of the Academy of Sciences of the USSR
Translated from Kinetika i Kataliz, Vol. 1, No. 1, pp. 5-14, May-June, 1960
Original article submitted December 16, 1959

The multiplet theory, which considers the structural and energetic factors in catalysis in connection with electronic concepts of organic theory, opens a way towards the understanding of the effect of the structure of molecules on the rate of heterogeneous catalytic reactions. The theoretical results which have been obtained are in agreement with experimental data recently obtained in the author's laboratory.

A basic theory of organic chemistry is that theory of structure in whose equations are considered the bonds between the neighboring atoms. This principle, which is to a large extent a geometrical one, has found a particularly clear application to stereochemical problems, and has been extended in an important way by the application of electronic concepts and the principles of quantum mechanics; through it, explanations have been provided, not only for strictly chemical bonds, but also for the mutual effects of atoms which are not directly linked together. Effects having such names as the homolytic and heterolytic mechanisms, the inductive effect, and the conjugation effect, come within the scope of such applications.

In the matter of homogeneous organic catalysis, a quantitative approach to the question of the effect of structure on the rate has been provided by a number of regularities developed by Brönsted, Hammett, and some others. Among these last can be reckoned the linear relationship recently observed by R. M. Flid[1] between the logarithm of the rate constant and the oxidation potential of the catalyst in reactions involving acetylene. In the homogeneous catalytic reaction, the formation has been observed of unstable intermediate compounds, such as the carbonium ion [2].

In heterogeneous catalytic organic reactions, the reactions themselves are simplified, especially in the case of the reactions of the doublet or triplet type [3]. On the other hand, the solid catalyst itself introduces a new factor into the consideration: the whole theory of the solid state is involved in this, especially that part which concerns the structural and electronic properties – which are, of course, inextricably bound up with each other. We shall here be concerned with the former of these. The atomic radius plays an important part in this connection, to which the Goldschmidt Rule bears witness.** The magnitudes of the atomic radii are the everyday tools of metallurgists and crystal-chemists.

The process of crystallization is of great importance in the preparation of catalysts. The activity of catalysts depends, above all, in an absolute sense, on the concentration of the nuclei formed during the preparation of the catalyst. A study of the ways in which the nuclei may be formed has been conducted by the author, V. I. Spitsyn, L. I. Barsov, and V. I. Duzkenkov [4] by irradiating solutions of platinum salts by means of electrons of energies up to 1,500,000 ev. In the course of this, platinum catalysts were obtained with an activity several

*A communication of the All-Union Conference on Organic Catalysis in Moscow, November 16, 1959.
**"The structure of a crystal is determined by the ratio of the numbers, the ratio of the sizes, and the polarization properties of its structural units" – V. Goldschmidt, 1929 [Translator's note].

times as great as is usually found (for such reactions as the hydrogenation of cyclohexene) when the catalysts are prepared by ordinary chemical reduction. Among the platinum complexes which have been investigated (Fig. 1), platinum could be obtained most easily from sodium pentahydroxychloroplatinate with trans-arrangement of Cl–Pt–OH.

Recrystallization is also an important factor in causing inactivation of catalysts.

Crystal growth, either normal or with dislocations, is usually accomplished through the precipitation of the material which forms the crystal. However, if crystallographical conformities are observed, it is possible to

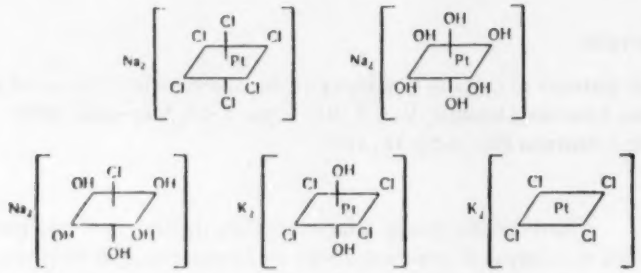


Fig. 1. Platinum complex compounds.

deposit a second substance on the first layer, and so grow a second phase on top of the first. This phenomenon is called epitaxia. It seems that epitaxia often exists between a catalyst and its carrier. Thus, for nickel on alumina, copper on chromic oxide, and rhenium on carbon [5], there is almost an exact whole-number correlation between the interatomic distances in the lattice of carrier and catalyst. In our laboratory, a study has been made of the formation of carbon on catalysts during the decomposition of organic compounds [6-8]. Carbon dendrites were obtained on the metals [9-10], which were also, apparently, definitely directed.

It is natural, therefore, to think that the catalytically active centers are the points at which crystal growth occurs. Adsorption which leads to catalysis can then be regarded as a kind of surface alloy formation between the molecules of the reacting substance and the catalyst. Frankenburg and Temkin arrived at a similar understanding of the role of the nitrogen in the synthesis of ammonia. During the catalysis, they suggested that instead of the deposition on the points of crystal growth of the substance of which the crystal consists, there was deposited a monolayer of molecules of the reacting substance, which then underwent chemical transformation.

In the main, what has here been suggested constitutes the multiplet theory of catalysis. Owing to the small radius of action of the valence-chemical forces, it is necessary for the reacting atoms in the molecule (the index group), and the atoms of the catalyst, to come into close contact in the activated multiplet complex. Hence, the emerge the principles of structural correspondence of this theory. Linked with this is the principle of energetic correspondence of the same theory, according to which, for the most effective catalyst, the quantities E' and E" in the following equations should be equal:

$$\left.\begin{aligned} E' &= -Q_{AB} - Q_{CD} + (Q_{AK} + Q_{BK} + Q_{CK} + Q_{DK}) \\ E'' &= Q_{AD} + Q_{BC} - (Q_{AK} + Q_{BK} + Q_{CK} + Q_{DK}), \end{aligned}\right\} \qquad (1)$$

where E' is the heat of formation, and E" the heat of decomposition of the intermediate complex M. Q is the energy of the links in the index group (a), which is transformed via M into the reaction product (b):

$$\begin{array}{cc} A & D \\ | & | \\ B & C \end{array} \quad (a) \rightarrow \quad \begin{array}{cc} A \cdots D \\ \vdots \quad \vdots \\ B \cdots C \end{array} \quad (M) \rightarrow \quad \begin{array}{c} A - D \\ \\ B - C \end{array} \quad (b) \qquad (2)$$

K is the catalyst. Equation (1), which was proposed by the author, has been arrived at since on other grounds by Temkin [11]. The activation energy, ϵ, is connected with E (the lesser of the two values E' and E") by the relation:

$$\varepsilon = 11{,}5 - \gamma E, \tag{3}$$

in which for endothermic reactions $\gamma = 0{,}75$, and for exothermic, $\gamma = 0{,}25$.

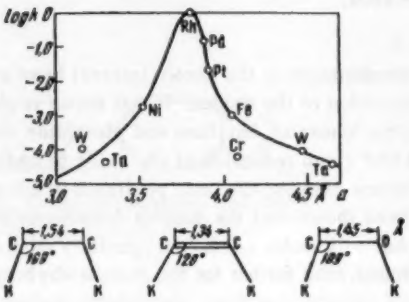


Fig. 2. Upper figure: relationship of the logarithm of the rate constant (log k) for the hydrogenation of ethylene, to the lattice constant a, of the catalyst (after Beeck [15]). Lower figure: interatomic distances and valency angles for the bonds: C−C, C=C and C−O in the activated complex during hydrogenation.

It is a consequence of the multiplet theory that the structure of the molecules (and of the catalyst) may affect the rate of reaction in at least three ways: (1) by changes occurring within the index group; (2) by changes occurring in the chain attached to the index group which does not make contact with the catalyst; and (3) by changes occurring in the chain attached to the index group when this lies along the catalyst surface. In each of the three cases, we have to consider the effect (1) on energetic, and (1) on structural factors.

The results which have been obtained in the author's laboratory during the last few years, subsequent to those published in 1957 [12] and 1959 [13], will also be studied.

The Intra-Index Effect for Doublet Reactions

We consider first the intra-index effect for doublet reactions. From a structural point of view, what is here intended is this: P. Teteni [14] and the author have found that, during the dehydrogenation of isopropyl alcohol (and other alcohols), the index group behaved in different ways when situated on metals with a single kind of surface structure (A1 and A3) but different interatomic distances D. The activation energy grows in a linear fashion with the latter. This functional relationship could have been expected from the point of view of the multiplet theory. On the other hand, no regularity was found between ϵ and d-character or the electronic work function.

The multiplet theory leads to the conclusion for doublet reactions [3] which can be called the principle of conservation of valence angle. Thus, for example, Beeck and his co-workers [15] found that the curve for the hydrogenation of ethylene gave a maximum for rhodium, when the logarithm of the activity was plotted as a function of D or the lattice parameter a (Fig. 2). Herington [16] showed that with an analogous model for the hydrogenation of acetylene, where the valence angle (120°) is greater than for the hydrogen of ethylene (109°), the optimum value of a was shifted to the right on the figure, in accordance with the theory. N. A. Vasyunina, S. V. Chepigo, G. S. Barysheva, and the author [17] have calculated that for the hydrogenation of the C=O bond, the optimum ought to be shifted in the reverse direction − that is, to the left − and should lie at ruthenium. This was based on the facts obtained by the same authors during the hydrolytic hydrogenation of the higher polysaccharides on ruthenium in an acid medium, when the celluloses gave the polyhydric alcohol sorbitol, and the pentosans gave xylitol. It is possible that these processes may acquire great practical significance in our country, where there are many forests whose waste products might be thus put to use for the public good.

The structural relationships during catalysis by the defect structures of W-bronze have been studied by N. P. Sokolova and the author [18]. The results of this have only recently been published. It was shown in the course of this work that the multiplet and electronic theories could be applied together, advantageously.

With respect to the energetic relationships, a number of confirmations have been obtained of the conclusions calculated from the equations of the multiplet theory for reactions with different indices which occur during the hydrogenation of complex compounds. The hydrogenation of monosaccharides (30 cases) has been examined by N. A. Vasyunina and the author [19]; that of organic peroxides and hydroperoxides (15 cases) by L. Kh. Freidlin, N. V. Nikiforova, and the author [20]; and that of furan derivatives by A. A. Ponomarev and the author (100 cases) [21], among other examples.

It is possible, by means of Eqs. (1) and (3) to predict the possibility of carrying out individual reactions from data concerning the activation energies of other reactions. Thus, for the oxides of the elements of the second group of the Mendeleev Periodic Table, V. A. Ferapontov, A. A. Tolstopyatova, and the author have used the activation energies of dehydrogenation, ϵ_2, and of dehydration, ϵ_3 of alcohols (determined by O. V. Krylov, S. Z. Roginskii and E. A. Fokina [23] in a flow system at 1 atm to show that the doublet dehydrogenation of hydrocarbons (activation energy ϵ_1) is practically absent on beryllium oxide and magnesium oxide, proceeds with difficulty on zinc oxide, and is perfectly possible on cadmium oxide. The calculation is carried out on the basis of the equation:

$$\varepsilon_1 = \frac{2}{3}(\varepsilon_2 - \varepsilon_3) + Q_{OK} - 48{,}6, \qquad (4)$$

which is derived from Eq. (1). Here the numerical value 48.6 is a combination of the known internal bond energies for the bonds A–B, etc.; Q_{OK} was determined from the heats of formation of the oxides. It was shown in the work of Ferapontov, Tolstopyatova and the author [22] that cyclohexane, cyclohexene, butylene and piperidine are actually dehydrogenated on cadmium oxide at temperatures around 500° (with reduction of the oxide to cadmium as a side reaction). This constitutes a case where the existence of a new catalyst has been predicted in advance of its use. In work by Rozhdestvenskaya and the author [24], it has been shown that the doublet dehydrogenation of hydrocarbons, especially of butylene, proceeds on pure zinc ozide, but only under conditions specially favorable to the reaction (for example, when the phenomenon of conjugation is found, read further for the reasons why butylene reacts). This also, therefore, is in harmony with theory.

Bond Energies for Yttrium Oxide and Those of the Rare Earths (kcal)

Catalyst	Q_{HK}	Q_{CK}	Q_{OK}
Y_2O_3	52,8	27,1	73,4
La_2O_3	49,7	3,8	78,5
CeO_2	57,6	11,5	49,9
Pr_2O_3	56,2	17,6	42,3
Nd_2O_3	78,3	12,2	56,6
Dy_2O_3	63,1	14,7	60,0
Er_2O_3	54,3	4,7	68,4

Levi, Broude, and the author have applied the equations of the multiplet theory to the decomposition of cyclohexanol on activated carbon as a catalyst, and concluded that of fifteen reactions which might be considered, this was the most likely to take place under these conditions. Their subsequent experiments have confirmed these predictions in the main, though with one considerable exception.

The kinetic method of determining the bond energies of reactants with catalysts is, of course, based on Eqs. (1) and (3), which contain two variables [3]. We have for this reason carried out a systematic assembling of the material [3] which would be needed for an intelligent selection of appropriate catalysts for particular reactions to be made. In this paper, we give some indication of the new data, especially for the rare earths lanthanum, cerium, praseodymium, neodymium, samarium, dysprosium, erbium, and also yttrium, in the form of their oxides: Me_2O_3. These are shown in the table, from the work of A. A. Tolstopyatova, A. A. Balandin and their co-workers [26]. Although this differs from the opinions of previous authors, it appears that the catalytic properties of the rare earths are very varied. We have also measured in our laboratory the bond energy for vanadium trioxide (with N. P. Sokolova [27]), titanium dioxide (with I. R. Konenko [28]), zinc oxide (with I. D. Rozhdestvenskaya [24]), and others. Kinerman and the author [29] have calculated the bond energies, not only of nickel, but also of iron, platinum and palladium, using the data published in the literature for the kinetics of a number of reactions. The application of these values of Q [30] to reactions involving cyclization or ring-breaking has been found to be in harmony with the experimental data obtained by B. A. Kazanskii and his collaborators.

Sextet Systems

We now move over to more complicated types – sextets – considered from the viewpoint of the multiplet theory. A résumé of the facts in support of the theory has been given recently [12]. In 1958, the Chemical Society of London published a Handbook of Interatomic Distances [31]. The regularity which had previously been found, according to which the cyclohexane ring is only disrupted on metals having lattices of the type A1 and A3, and with definite interatomic distances lying between 1.24 and 1.39 A, has been confirmed by the study of these new, accurate data. An exception is found in the case of copper, but the conclusion to be drawn from this is not that the multiplet theory is disproved, but only that the simple consideration of structural factors is not sufficient in this case: energetic factors must also be taken into consideration. Technetium, which has an A3

lattice with r = 1.351 A should act as a catalyst for the dehydrogenation of cyclohexane, but this has up to now not been demonstrated. On the other hand, the predictions of the multiplet theory have been confirmed in the case of rhenium, for which it was anticipated that it would behave as a sextet catalyst for the dehydrogenation of cyclohexane (E. I. Karpeiskaya, A. A. Tolstopyatova, and the author [5]). The most active form of rhenium catalyst consists of rhenium deposited on carbon [5]. It seems also that rhenium will produce irreversible catalysis of cyclohexene. Kinetic investigation has shown that the irreversible catalysis on rhenium often proceeds more slowly than the dehydrogenation of cyclohexane [32], which shows that the sextet dehydrogenation cannot take place in a stepwise manner through irreversible catalysis, as has been supposed by M. Ya. Kagan and others [33].

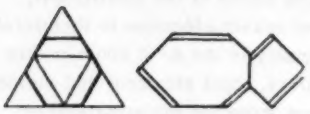


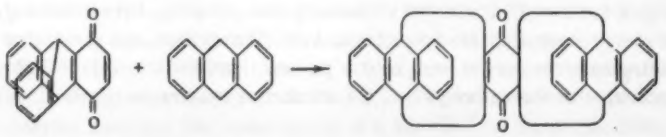
Fig. 3. Sextet scheme, and the structural formula of azulene.

According to Plattner and his collaborators [34], dehydroazulene is only dehydrogenated with difficulty on a palladium catalyst (to the extent of 30%, the remainder being decomposed). Azulene has an aromatic character: that is, dehydrogenation increases the degree of conjugation. It appears, however, that this is insufficient, and for dehydration, the presence of some favorable factors is necessary: azulene cannot be superimposed on the sextet in the same way as benzene or cyclohexane (Fig. 3). These facts are in harmony with the expectations of the multiplet theory. The small percent of dehydrogenation on palladium catalysts is presumably to be explained by the occurrence of a doublet mechanism, such as is already known for this catalyst [35]. On films of tungsten, which has an A2 lattice, benzene is hydrogenated according to a doublet mechanism, as can be seen from the work of Anderson and Kemball [36].

Effect of the Nature of Side Chains

We turn now to the influence of the nature of the side chain on the catalytic process. In a number of cases, the length of the side chain attached to the index group has little or no effect on the rate or activation energy of reactions of a given type. Such cases are, for example, the dehydrogenation of alcohols on copper catalysts, as observed by Palmer and Constable (see [12]). Brihta and Luetic [37], Teteni and the author [14], and especially the detailed information obtained quite recently by O. K. Bogdanov, A. P. Shcheglova, and the author [38] for normal alcohols from C_2 to C_9 on oxide catalysts. From a structural standpoint, this would be explained in this way: when the alcohol undergoes reaction, it is oriented at the surface in such a way that its reacting group, >CHOH is located on the surface (which is in harmony with the multiplet theory), while the hydrocarbon part of the molecule is oriented perpendicular to the surface of the catalyst in a similar manner to that found in a Langmuir film. This would be the case for chains attached to the index group if they are not themselves in contact with the catalyst. From the energetic standpoint, the observed constancy of rate denotes the compensation of the effect of substitution on the energy of the intra-index bond, Q_{AB}, by the effect of the same substitution on the bond formed between the atom A and the catalyst, Q_{AK}, using the nomenclature of Eq. (1).

The question arises, however, whether in the case under consideration, steric hindrance may not arise: that is, whether large substituents may constitute a structural hindrance to the necessary contact between the atoms of the index group and the catalyst surface. The answer might seem to be in the affirmative, since cis-olefins, which are able to turn towards the surface in a large number of ways, are hydrogenated more easily than the trans olefins. But the substituted triptitsenes, as was found by Klabunovskii and the author [39], in spite of their complex shape which would not permit of close conformity with a smooth surface, are nevertheless hydrogenated on a nickel catalyst under gentle conditions. This suggests that the active center is in the form of a projection, side by side with which is a hollow into which the projecting part of the adsorbed molecule may fit. If the superimposition takes place in this way, it is then possible to estimate the dimensions of the active centers. Thus, in an investigation of the kinetics of the hydrogenation, Klabunovskii and the author [40] first synthesized dianthrylenedihydrobenzoquinone,



and then submitted it to hydrogenation, finding thus that the active centers on nickel should be not narrower than 4.8 A, and the hollows not deeper than 3.17 A (Fig. 4).

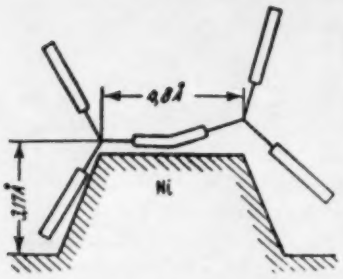


Fig. 4. The superimposition of dianthrylenedihydrobenzoquinone on an active center of a nickel catalyst during hydrogenation.

Other cases exist in which mutual compensation does not take place between the effect of the substituent on the energy of the bond linking the atom A with the molecule, Q_{AB}, and the energy of that linking the atom A, with the catalyst, Q_{AK}. In such a case the nature of the substituent will affect the rate of the reaction. In the first place, as in ordinary organic chemistry, one must estimate the inductive effect, the physical meaning of which will be that the atoms of the substituents, depending on their nature, either attract electrons to themselves, thus diminishing the electron density in the A–B bonds within the index group, or, on the contrary, repel electrons and increase this electron density. It is known, from the investigations of A. V. Lozovoi and his colleagues [41, 42], that the same substituent may exert opposite effects on the rate of hydrogenation of the alkyl benzenes, depending on the catalyst (nickel on alumina on the one hand, and molybdenum disulfide on the other). In the former case, increase in the number of substituents causes a reduction in the rate, and in the other an increase. This points to a noncompensating effect of the substituents on the energies of the A–B and A–K bonds.

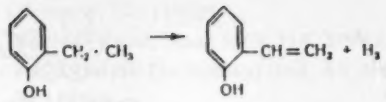
The effect of substitution on the activation energy has been studied for the removal of the elements of water from alcohols by Doze, I. V. Adadurov, A. Kh. Bork, and A. A. Tolstopyatova (for a résumé see [43]), using oxides of aluminum and tungsten, and for the dehydrogenation of alcohols by oxide catalysts by O. K. Bogdanova, A.P. Shcheglova, and the author [44]. It has been found that α- and β-substitution of the methyl groups exercises an additive effect on the activation energy.

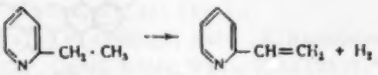
N. A. Vasyunina and the author have considered the hydrogonolysis of polyhydric alcohols on a nickel catalyst [19], and have calculated on the basis of Eq. (1) that the C–C and C–O bonds should be affected differently according to their positions in the molecules: 1) the C–C bond in the middle of the hydrocarbon chain of the molecule should be the easiest of all to rupture; 2) the ease with which this rupture occurs should diminish stepwise as the bond considered approaches nearer to the ends of the chain; and 3) the C–O bonds in the primary positions should be broken more easily than those attached to secondary carbon atoms. These conclusions have been confirmed by around thirty different reactions involving hexitols, pentitols, erithrytol, etc., which have been obtained by the hydrogenation of sugars (see above). This last reaction itself provides a good example of the usefulness of the multiplet theory.

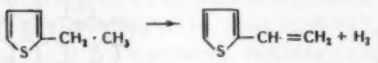
In the case of the induction effect, the substituents exert an influence on the bond energy in the index group, and consequently, on the rate of the reactions. The effect is analogous to the auxochromic effect on the chromophoric group in the theory of color. Langenbeck [45] arrived at a similar concept in studying enzyme models.

Thus, up to a certain point, the effect of substituents is quantitative rather than qualitative. In connection with this we would point out that the dehydrogenation reactions, proceeding through the doublet index group:

occur widely among a number of substances containing this grouping, but containing, in addition, different substituents. In the recent work of O. K. Bogdanova, A. P. Shcheglova, and the author [46], a method has been worked out of obtaining isoprene on the basis of this process, and in the work of G. M. Marukyan, I. I. Brusov, A. D. Petrov, and others, with the author [47-48], a number of monomers similar to styrol have been obtained:







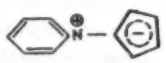
$$CH_3 \cdot CH_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot Si(CH_3)Cl_2 \rightarrow$$

$$\rightarrow CH_2{=}CH \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot Si(CH_3)Cl_2 + H_2$$

$$CH_3 \cdot CH_2 \cdot C_6H_4 \cdot Si(CH_3)_3 \rightarrow CH_2{=}CH \cdot C_6H_4 \cdot Si(CH_3)_3 + H_2$$

In addition to the induction effect, another effect which can influence the behavior of the side chains is the conjugation effect. The physical meaning of this is the interaction of the π-electron clouds of the conjugated multiple bonds.

M. L. Khidekel', V. V. Patrikeev, and the author [49] have studied the effect of the conjugation energy σ, on the kinetics of hydrogenation reactions on a rhodium catalyst (containing 0.1 to 2.5% rhodium on alumina), in solution at 5-60° and 1 atm. The reactions were found to be of zero order. Comparison of the data for different compounds under similar conditions has shown: 1) that increase of σ for the reacting substance results in a diminution of the rate constant $\underline{k}$ of the reaction; 2) that when the values of σ differ only slightly, the induction effect is strongly apparent; and 3) that the nature of the solvent has no decisive effect. However, if the solvent disturbs the aromatic character of the compounds, this may lead to a sudden increase in the constant $\underline{k}$. Thus, using N-pyridinium cyclopentadienilide in alcoholic solution under constant conditions, k = 7.8 ml/min, while in acetic acid k = 24.0 ml/min (for the first two moles of hydrogen). When the cyclopentadiene was replaced by benzene, the corresponding values of K were 8.0 and 10.2 ml/min, respectively.



When adsorption on to the catalytically active centers occurs, part of the conjugation energy is lost. Usually, if the reaction is accompanied by loss of conjugation energy, it is impeded on this account, while if the conjugation energy increases the reaction is facilitated. If two substances, 1 and 2, are considered under the same conditions, we have found that:

$$\lg \frac{k_2}{k_1} = a(\sigma_1 - \sigma_2) + b, \quad (5)$$

where $\underline{a}$ and $\underline{b}$ are constants. The application of Eq. (5) is shown in Fig. 5. It is possible to arrive at the equation on theoretical grounds. For more detail see [49].

Finally, a third way in which the structure of the molecules may influence the course of catalytic reactions is the superimposition of the side chains on the catalyst. This is, it would seem, the way in which enzymes function. This view is based, on the one hand, on results obtained by, V. É. Vasserberg, M. P. Maksimova, and the author [50], which show that the adsorption of alcohols of various chain lengths on alumina at low temperatures does not proceed by way of vertically oriented side chains in the way already discussed, but along the plane of the catalyst. Similar results were obtained by A. V. Kiselev and his collaborators [51] for the adsorption of alcohols on carbon black. We are reminded also of the results obtained by Mexted [52] on the poisoning of the catalyst by 1,4-propanedithiol. The view is considered also, on the other hand, because a number of catalysts with active centers also show hollows between them (E. I. Klabunovskii and the author, see above). It appears that fermentation reactions, with respect to the index groups involved, are double or triplet reactions (the author [53]). We may therefore suppose that in enzyme catalysis the index groups are adsorbed on the projections, and the substituents

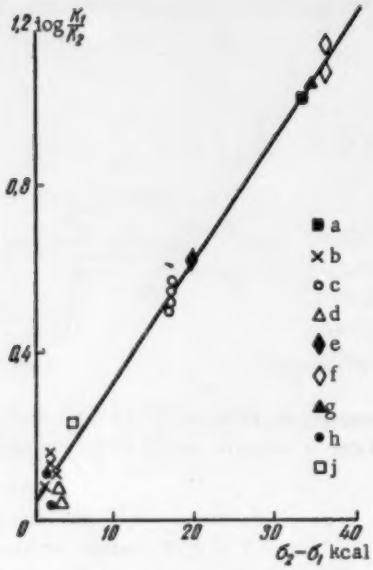


Fig. 5. Relationship between the conjugation energy and the rate constant for hydrogenation on rhodium: a) for cyclopentadiene and benzene; b) for eugenol and cis-isoeugenol; c) for dihydrofuran and furan; d) for cyclopentene and cyclopentadiene; e) for furan and benzene; f) for cyclohexadiene-1,4 and benzene; g) for cyclohexadiene-1,3 and benzene; h) for cyclohexadiene-1,4 and cyclohexadiene-1,3; j) for diphenylmethane and diphenyl.

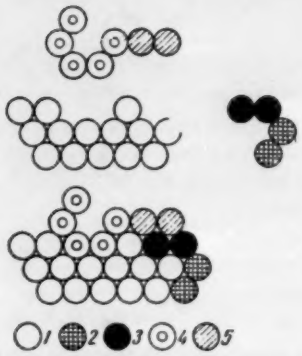


Fig. 6. Scheme for enzyme catalysis: 1) Protein part of the enzyme; 2) co-enzyme; 3) active centers; 4) side chains; 5) index group of the substrate.

attached to the index group are adsorbed in the hollows, probably by means of hydrogen bonds. The large degree of structural correspondence explains the particularly high selectivity, and the high activity which arises from the reduction of activation energy on account of the adsorption of a substance similar in its type to the substrate. Adsorption at three points, such as takes place in this case, will also explain the occurrence of asymmetric synthesis. A schematic model of enzyme reactions is given in Fig. 6. Symbols with different headings are used to denote the albuminous part of the enzyme, which combines with the coenzyme, and the substrate which is superimposed on them. Similar models have been used to denote the action of antimetabolites. These suggestions, published in papers [53, 54, 55] on the basis of the multiplet theory, were arrived at practically simultaneously by the Swiss, Dreiding, and published by him in [56]. It is obvious that there must be other effects, based upon the effect of structure in the way discussed above, which take place in fermentation catalysis.

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AN INVESTIGATION OF THE PART PLAYED BY ELECTRONIC FACTORS IN CATALYSIS*

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It has been shown for a number of catalysts that changes in the catalytic properties produced by modifying additives is due to electrostatic charging of the surface, and that the changes in E_{cat} and E_{chem} which take place under these circumstances are a linear function of changes in the electronic work function. A regularity has been found connecting the electronic properties of new semiconductors with their catalytic activity. A theory of the effect of the charge on catalysts on homogeneous and heterogeneous surface properties is developed.

There is a scarcity of systematic data concerning the part played by electronic factors in catalysis, and it is impossible to carry out quantitative quantum mechanical calculations of even the most simple chemical processes which take place on solid surfaces. For this reason the generalizations advanced by a number of authors under the name of "electronic theories of catalysis," is based on very much simplified models and premises derived from related fields of study, with the addition of supplementary, and arbitrary, hypotheses. While recognizing the stimulating value of these generalizations, it is not possible without purposeful experimental investigations to estimate what part of the hypothetical structure which has been developed is really valid, or what is the true role of electronic mechanisms in heterogeneous catalysis.

Such experimental investigations have been conducted in our laboratory for a number of years, using complicated electronic and isotopic methods, in the course of which attention has given to catalysis on contemporary semiconducting materials which have well-established physical properties. In addition to that, work has been carried out on semiconductors which have been modified by the addition of materials whose valence is different from that of the main atoms or ions in the crystals employed [1].

Part I: Electronic Factors in the Activity and in the Selection of Catalysts

1. The nature of the charge on the adsorbed layer. In electronic theories of catalysis on semiconductors [2, 3] and metals [4], great significance is attached to the charge existing on the adsorbed molecules, produced by the displacement of the surface electronic levels. For solid materials in contact with a gaseous medium, the easiest method of determining the surface charge is to determine the change in the work function $\Delta\varphi$, by means of the contact potential difference ΔV_C. This consists of two components: the change in the diffusion potential ΔV_D, which characterizes the magnitude of the curvature of the zone, that is, the charge of the surface in relation to the volume of the semiconductor; and Dip, or the potential jump at the surface itself, caused by the dipole moments of the adsorbed atoms and molecules. When gas is dissolved in the catalyst lattice, or when

*The basis of a communication presented to the Second International Congress on Catalysis.

additives are supplied to it, or when its structure is ruptured, a third volume component, $\Delta\varphi_{vol}$ must be introduced, which may be formally characterized in the simplest case by the displacement of the volume Fermi level $\Delta\mu_{vol}$ within the limits of the zone under consideration (Fig. 1).*

$$\Delta\varphi = \Delta\varphi_{ads} + \Delta_{vol} \Rightarrow \Delta V_D + Dip + \Delta_{vol} \quad (1)$$

TABLE 1

Charge on Adsorbed Molecules as Determined from Values of $\Delta\varphi$ and $\Delta\sigma$

Catalyst	Adsorbate							
	O_2	CO	H_2	C_2H_4	C_2H_5OH	C_3H_7OH	$(CH_3)_2CO$	C_6H_6
NiO	—	+	A. L.	+	+	+	+	+
CuO	—	+	A. L.	+	+	+	+	+
ZnO	—	A. L.	A. L.	N. M.	+	+	+	+
V_2O_5	—	+	+	+	+	+	+	+
Ge, (*n*, *p*)	∓		+	N. A.	+	+	+	+
Mn_2CoO_4	—	—		+	+			
Co_2MnO_4	—	—		+	+			
Ag	O_2^-	$C_3H_6^+$	H_2 A. L.					
Fe industrial	O_2^-	$H_2^\mp$	N_2^-	CO^-	CO_2^-	NH_3^+	H_2O^-	

Note. A. L. =adsorbed layer; N. M.= not measured; N. A. = not adsorbed.

Table 1 shows that in the majority of cases, $\Delta\varphi_{ads}$ for semiconductors $\neq 0$; that is, the adsorbed molecules are charged, and more often than not the charge is positive. Olefins, alcohols, benzene, and others carry a positive charge, and oxygen a negative. It is usually found that the sign of the charge on the surface is independent of the type of semiconductivity, and is determined by the existence of donor or acceptor properties in the adsorbed molecules [5]. No such definite behavior is found in the case of hydrogen, for which positive, negative, and practically zero charge may be observed. Anomalous sign for the charge is also observed in the case of carbon monoxide. According to the data obtained by us on iron and silver (base of Table 1), the evidence is that negative charges are most common on metal catalysts. The same type of evidence is provided for a large number of different molecules in the first adsorption layer, as determined by electron emission in projectors [6, 7]. The charge of the surface is preserved during the course of the reaction, and according to the change in ΔV_c may continue subsequently to this [8]. It is usually found on semiconductors that Dip << ΔV_D; but on metals which are not covered with films, this division into two components loses its meaning. When fully ionized additives are present in n- and p-semiconductors, the process which lies at the basis of the charging of the surface through adsorption may be represented graphically as the removal of a certain number of current carriers from the pre-surface layer, or, alternatively, as the enrichment of the number of current carriers present there Fig. 2). With the occurrence of this "stoichiometric" transfer of electrons on any given conductor for various degrees of covering θ, the value of $\Delta\varphi$ produced by the various molecules having the same sign of charge should coincide. In reality, for a given value of θ the values of $\Delta\varphi$ may differ several fold (Fig. 3), and the absolute values of $\Delta\varphi$ obtained experimentally are considerably lower than those expected for an ideal semiconductor surface with known values of the screening length. V. B. Sandomirskii and Sh. M. Kogan offer an explanation of this divergence in terms of the presence of structural defects

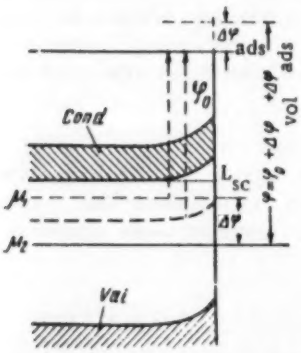


Fig. 1. Diagram to show the explanation of the origin of the work function, φ, of a semiconductor, and its change when adsorption of an acceptor gas occurs ($\Delta\varphi_{ads}$); together with the transition from mixed to simple conductivity ($\Delta\varphi_{vol}$); L_{sc} = thickness of screening zone.

*If the characteristics φ and $\Delta\varphi$ are obtained by means of photoemission, it is possible to obtain the local values for sections of the surface of different activity.

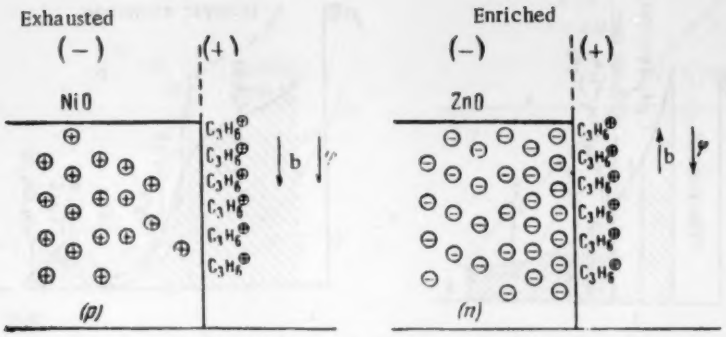


Fig. 2. A quasistoichiometric model of the change in the surface concentration of holes (⊕) and electrons (⊖) during the chemisorption of donor molecules of propylene on a p- or an n-semiconductor.

in the surface, and of impurities, which constitute pockets of disturbance in the surface electronic equilibria, and also the presence of assemblies of different surface levels [9]. When adsorption takes place of mixtures of uniformly charged substances, these have the effect of diminishing the effect of each other's adsorption, while differently charged substances have the opposite effect.

2. Nonuniformity, and its connection with the electronic behavior of solids. The investigation of a series of systems using specially developed isotopic methods [10] leaves no room for doubt as to the reality, abundance, and importance of catalytic phenomena in which the catalytic properties are influenced by biographical nonhomogeneity of surfaces [11]. In particular, this has been directly shown by N. P. Keier for the hydrogenation and decomposition of acetylene on nickel [12]; and by O. V. Krylov and E. A. Fokina [13] for the decomposition of isopropyl alcohol on basic and acidic catalysts (Fig. 4b). It has been convincingly shown in recent years that certain semiconductors possess surfaces which are nonuniform with respect to their energy levels, and also with respect to the time at which current carriers are present on them [14]. The nonhomogeneity of the catalysts is due to the different catalytic properties of facets possessing different indices [15-17], to impurities [18], and to structural defects, among other causes.

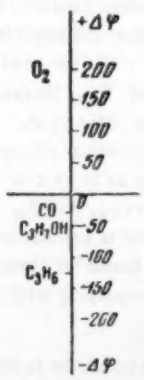


Fig. 3. Isosteric change of the value of φ for cupric oxide on adsorption of various gases. $N_{ads} \cong 10^{12}/cm^2$.

In analyzing the nature of chemical processes taking place at a surface, the charge and nonhomogeneity of the surface may, to a first approximation, be considered as two independent factors, which must be retarded as operating simultaneously. At the same time, experiments carried out using solid solutions, and oxides with modified surfaces, as catalysts, show that the electronic disturbance caused by the exchange of cations or atoms in the lattice by foreign cations or atoms with a different valency [19] may increase the nonhomogeneity of the surface and alter its character. The foreign atoms which possess an anomalous valency create a polyatomic region in the semiconductor in which there is an increased probability of the presence of free electrons, or, in the alternative case, of free holes. The probability of any electronic process on such a surface will change gradually with the distance from the foreign atom. Adsorption accompanied by charging of the surface would take place in a similar way. Hence, though with very large approximations, it is possible to take into account the mutual influence of charging and nonuniformity. With complicated contacts, the sign and magnitude of the charge on the molecules may be different on crystallites of various phases and on the various portions of the nonhomogeneous surface.

3. Electronic properties and modification. There are many ways in which the addition of other materials may change the properties of a catalyst, but the one which presents the greatest interest is the so-called modification [20], by means of which either the nature of the catalytic effect or the specific activity of the catalyst is altered [21]. Numerous investigations have been carried out in several countries on the basis of oxide catalysts, and have shown that the replacement of atoms or ions in the crystal lattice by other atoms or ions having a different valency constitutes one of the most effective means of bringing about modification.

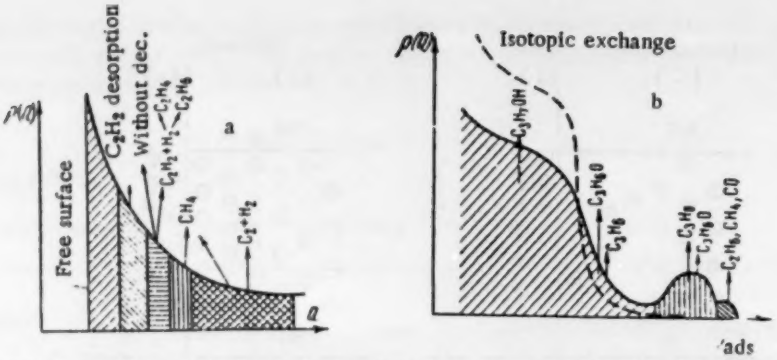


Fig. 4. a) Plan of distribution according to the heats of adsorption of molecules taking part in various reactions of acetylene chemisorbed on nickel; b) the same for various reactions of isopropyl alcohol on calcium oxide.

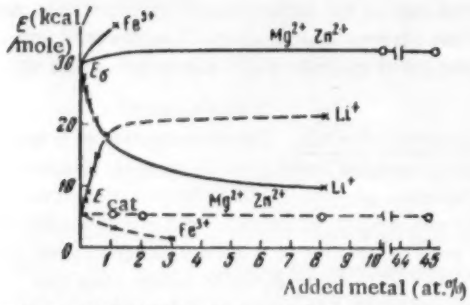


Fig. 5. The change in E_{cat} (solid lines) for the reaction between carbon monoxide and oxygen on nickel oxide, under the influence of different modifying additives; the change in E (broken lines) for the same systems.

The same procedure is widely used for the control of the electrical conductivity and other electronic properties of semiconductors. The importance of the electronic disturbance in bringing about these changes has been confirmed by the fact that the initial activity of zinc oxide and nickel oxide catalysts is not altered if foreign ions of the same valency are dissolved in these oxides* (Fig. 5) [22].

The work of É. Kh. Enikeev, L. Ya. Margolis, and others has shown, both for disruptive and for other types of contact modification, that a simple linear relationship, may, in a number of cases, be developed between the activation energy of the chemisorption, E_{chem}, or of the catalytic process E_{cat}, on the one hand, and the electronic work function φ, on the other. It is often found that the changes in E and φ are numerically close to each other [23, 24]. The electronic work function is a considerably better measure of the electronic nature of the modified catalyst than is the electrical conductivity. This is illustrated for the oxidation of carbon monoxide on nickelous oxide catalysts with various additives, and for the chemisorption of oxygen on zinc oxide in Figs. 6a and 6b, respectively. In the former case, E_{cat} increases linearly with reduction in the work function, while in the latter, E_{chem} increases linearly with increase in φ. The change in E, connected in both cases with the change in φ, leads at a constant value k_0 to enormous changes in the rates of the catalytic processes. The value of $\underline{k}$ is, in fact, usually not constant, changing by at least 1-3 orders of magnitude on account of the strong compensation effect [27]. The relationship between E_{cat} and E_σ for the electrical conductivity (σ) is not as simple as those just given (see Fig. 5 and Fig. 6a), and is insufficient to explain the magnitude and sign of $\Delta\varphi$. For complex systems, the correlation which has been found for simple cases between $\underline{k}$ and σ is usually lacking. Hence, ΔE_σ and $\Delta\sigma$ are less suitable than $\Delta\varphi$ for comparison with the activity of the catalysts.

The examples which have been considered relate to semiconductor catalysts. A similar relationship is found for iron catalysts used in the ammonia synthesis [28] (see Fig. 7). The selectivity of the oxidation of ethylene into ethylene oxide on silver catalysts is also found to change in a linear fashion with $\Delta\varphi$, within certain limits [29].

4. Electronic factors in the selection of catalysts. The question as to the part played by electronic factors in the selection of catalysts has been elucidated by the work carried out by our collective in the laboratory of

*There are discrepancies between the results obtained by different authors in studying these systems [25, 26, 1], the reasons for which are not clear.

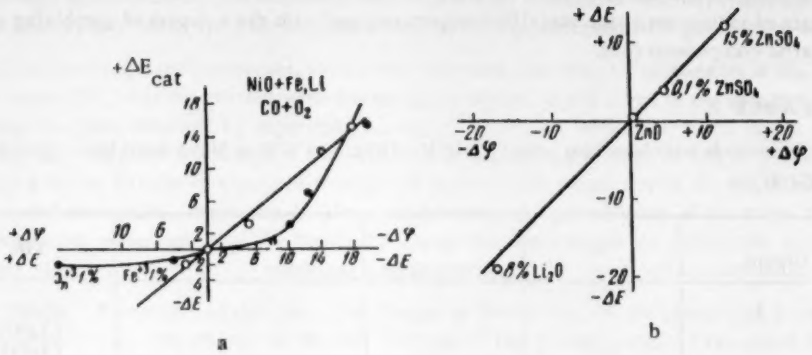


Fig. 6. a) Relationship between E_{cat} for the reaction $2CO + O_2 \rightarrow 2CO_2$ on nickel oxide and ΔE_σ in the presence of modifying additives; b) relationship between ΔE_{chem} for oxygen on zinc oxide and $\Delta\varphi$ in the presence of modifying additives.

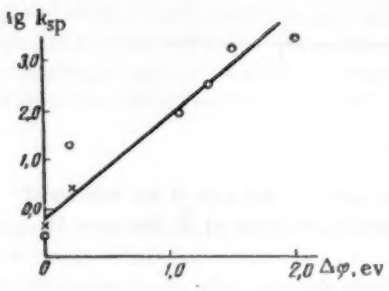


Fig. 7. Relationship between log k_{sp} and $\Delta\varphi$ for promoted iron catalysts in the ammonia synthesis.

Professor Shvab, and others, on the long-known, and very important (but not universal) connection between high catalytic activity of metals in hydrogenation and related reactions, and the presence (and number) of unoccupied d-orbits in the atoms forming the lattice, which has revealed new regularities:

1. Semiconductors with a similar type of electronic structure behave similarly with respect to catalysis. For example, germanium and silicon, and many binary compounds containing, on the average, 2s- and 2p-electrons on the atoms of the lattice (such as GeAs, InSb, ZnTe, Ga_2Se_3 and others) act as catalysts for the same reactions [30, 31]. All these semiconductors are also similar with respect to their physical electronic properties. They crystallize in lattices of similar types (close to that of diamond), in which all the atoms are linked together by covalent hybridized sp^3-bonds. Table 2 gives the interatomic distances in crystals isoelectronic with germanium, together with their electronic characteristics. Table 3 shows the position occupied in the periodic table of the systems which we have examined.

TABLE 2

Change in Properties of the Isoelectronic Series Based on Germanium and Zinc Blende (of structures diamond and sphalerite, respectively)

Substance	Lattice constant, A	Breadth of forbidden zone, ev	Substance	Lattice constant, A	Breadth of forbidden zone, ev
Ge	5,647	0,78	α-Sn (gray)	6,46	0,1
GaAs	5,64	1,53	InSb	6,46	0,24
Ga_2Se_3	5,43	1,8	In_2Te_3	6,14	1,0
ZnSe	5,65	2,80	CdTe	6,41	1,45
CuBr	5,68	2,94	AgI	6,47	2,80

2. It is seen from Table 3 that all these new semiconductors which will catalyze reactions of the oxidation-reduction type contain no transition elements.

In the zone theory, the initial electron-physical characteristics of a semiconductor are determined by the breadth of a forbidden zone $\mathfrak{A}$, which is systematically connected with the position in the periodic table of the

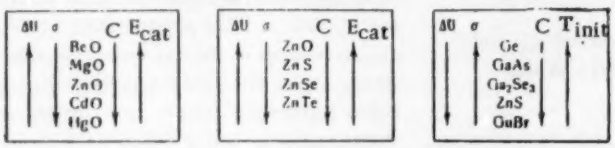
elements which form the semiconductor. Within the bounds of each of the isoelectronic groups, $\mathfrak{A}$ is associated with the energies of ionization of the metallic components, and with the energies of combining with the electron of the nonmetallic components [32].

TABLE 3

Compounds with Wurtzite and Sphalerite Structures Which Have Been Investigated as Catalysts

Groups	IV	V	VI	VII
I				(CuBr) (AgBr) (AgCl)
II			ZnS CdSe MgO ZnSe CdTe ZnO ZnTe HgS CdO CdS BeO HgO	
III		GaAs AlSb GaN InAs InSb	Ga_2O_3 Ga_2Te_3 Ga_2S_3 Ga_2Se	
IV	Ge Si		GeO	

3. As has been shown in [33], for the dehydrogenation of alcohols, the catalytic activity of the analogs of germanium increases, and the energy of activation diminishes, with reduction in the value of $\mathfrak{A}$ (Scheme 1).



Scheme I

Part II: Kinetics and Mechanism

1. Stages. The electronic factors in the kinetics of heterogeneous catalysis may be revealed: 1) in the appearance of additional stages showing the characteristics of an electronic mechanism; 2) in the nature of the interaction between catalyst and substrate; 3) in the effect of the surface charge of the catalyst on the process; 4) in the specific effects of remote action. The effect of electronic factors should be particularly strongly revealed when the reactions are carried out under purely kinetic conditions [34]. To the scheme of stages in the projection theory of catalysis must be added the electronic processes occurring in the solid body and the new stages in the molecules undergoing conversion. It has been assumed up to now that the former are always appreciably more rapid than the chemical stages of catalysis, and they have been taken into account only as auxiliary transitions, governing the equilibrium concentrations of the current carriers and the surface charge. According to A. F. Ioffe [35], this includes semiconductors with low mobilities as current carriers, for which an activation energy is needed even for the transfer of free electrons within the lattice (such as nickelous and ferric oxides). For germanium and silicon, on whose surfaces oxidized films are present, part of the transfer of electrons between the volume of the semiconductor and its surface takes place slowly and requires an activation energy [14, 36]. Such phenomena ought to be encountered frequently. Thus, the investigations of the surface diffraction of slow electrons carried out in the outstanding works of Farnsworth [37], and the emission images of monocrystalline points in electron projectors [6, 38] have shown that it is only with great difficulty that effectively clean surfaces of pure monocrystals of metals can be formed, in all gases except the inert gases, even at pressures as low

as 10^{-5} to 10^{-6} mm Hg. Even under such conditions, there is normally formed an ordered, stable surface layer some 1-2 atoms (or molecules) thick [7]. Similar phenomena have been observed with germanium and silicon.

Under conditions in which catalysis occurs, the surface ordered film may be covered by a less stable, amorphous sorption layer [37], making contact with thicker oxide layers, liquid films of the reagents, carbon films, and, according to results obtained by experiments using C^{14} as tracer, labile polymeric layers as well [39]. These data taken together oblige us to recognize the existence of an additional possible stage, governing the entire process, which consists of the transfer of electrons through the surface film which covers the conductor during chemical adsorption and desorption. When this is taken into account, the general plan of the stages through which the process goes (neglecting transport) takes the form: 1) electronic processes in the solid body, preliminary processes leading up to: 2) chemisorption; 3) chemical transformation of the chemisorbed molecules: 4) desorption.

2. Effect of charge. The effect of the electrical charge on the surface on the kinetics of a reaction is a combination of two phenomena: the change in the free energies of the processes which take place through the exchange of electrons between the solid body and the molecules (under the influence of the over-all macroscopic charge); and the change in the reactivities of the adsorbed molecules (owing to the polarization of bonds or the ionization of the molecules). At present only the former of these two effects has been investigated systematically, although the latter is probably the more important for understanding the essential mechanism of catalytic reactions and the treatment of complex processes. A kinetic equation for heterogeneous catalysis ought to express the relationship between the reaction rate, $\underline{w}$, and the temperature, and the concentration of the initial substances (c_A, c_B) and of the reaction products (c_C, c_D), as well as on the concentration of foreign substances (c_X, c_Y) which exercise an influence on the rate of reaction, or on their degree of surface saturation (θ_X, θ_Y). For reactions proceeding by way of a transitional complex (#) formed on the i-th group of active centers on a nonhomogeneous surface, the initial equation can be written thus:

$$w_i = \xi\theta_i^{\#} n_{0i} = k_{0i}^0 \exp\{[(\gamma RT - 1)/RT] E_i\} f^{\#}(\theta_{i\,ads} c_B \ldots) = \\ = k_{0i}^0 \exp(\Gamma E_i) f^{\#}(\theta_{i\,ads} c_B \ldots), \qquad (1)$$

where ξ is the frequency of the transformation of the transition complex #; $\theta_i^{\#}$ is the degree of saturation of the i-th portion of the surface by these; $n_{0\,i}$ is the number of the i-th active centers; $\exp[(\gamma RT - 1)/RT] \equiv \Gamma$, the compensation factor when $k_{0i} = k_{0i}^0 \exp(\gamma E_i)$; $f^{\#}$ is a concentration multiple of the type $\theta_{i\,ads}^{\nu\theta} \cdot c_A^{\nu A}$ for the transition complex, when this is formed from ν_θ molecules adsorbed on the i-th centers, and ν_A are the free molecules participating in the formation of the transition complex directly from the gas phase. The analysis of the effect of the charge V_S is included in the setting up of the relationship between this and E_i, $\theta_{i\,ads}$ and k_{0i}^0. For this purpose it is necessary to know: 1) the static charge isotherm for the mixtures, $V_S = V_S(\theta_A \ldots, \theta_C \ldots, \theta_X)$; 2) the effect of the charge on the static and kinetic isotherms for the adsorption of the mixtures, and on the activation energies. However, even for $V_S(\theta)$ for the adsorption of individual substances on a semiconductor, in the works based on the theory of the boundary layer [2], the conclusions arrived at are contrary to the experimental evidence unless special assumptions are made. The situation is no better for adsorption on metals than it is for that on semiconductors. It is better at present, therefore, to start from equations of a relatively empirical character, which can be systematically investigated for individual substances, and then applied to mixtures. It has been discovered in a series of studies [46] that:

$$Q_{ads}^{\pm} = Q \pm \Delta Q^{\pm} \cong Q \pm \beta\Delta\varphi, \qquad (2)$$

to which the corresponding equation for the adsorption coefficients is $a^{\pm} = a \exp(\pm\beta\Delta\varphi/RT)$. Using the connection established by Bronsted between E and Q of Eq. (2), we arrive at Eq. (3):

$$E_{ads}^{\pm} = E \pm \Delta E^{\pm} \cong E \pm \alpha\Delta\varphi. \qquad (3)$$

If Q, E and $\Delta\varphi$ are expressed in the same units, then $0 < \alpha < \beta < 1$. As we have shown on p. 16, and in Figs. 6 and 7, the relationship (3) for modified catalysts is fulfilled for the chemisorption on semiconductors, and for chemical reactions on both semiconductors and metals. Since the application of the general theory of semiconductors leads to the Shottki equilibria for the transitional surface complex, formed on a charged surface [40], we shall take Eqs. (2) and (3) as the basic relationships for obtaining the results of the kinetic equations employing the experimentally determined relationship between $\Delta\varphi$, and θ and $\underline{c}$. For reversible and irreversible adsorption, which take place with increase of current carriers on the semiconductor, when $\Delta\varphi > kT$, the relationship between

φ and θ is usually close to logarithmic, while for adsorption leading to reduction of the current carriers, the relationship is approximately linear [5] (see Figs. 8 and 9).

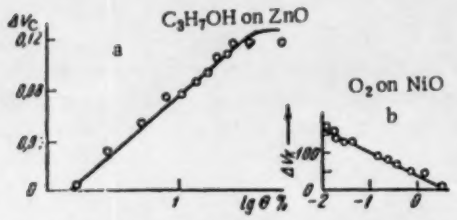


Fig. 8. Examples of logarithmic relationship between ΔV_C and θ for adsorption enriching the surface with current carriers. For (a) ΔV_C is given in volts, and for (b) in millivolts.

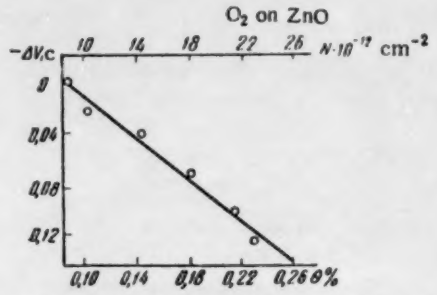


Fig. 9. Example of the linear relationship between ΔV_C and θ for the impoverishing adsorption of oxygen on zinc oxide (volts).

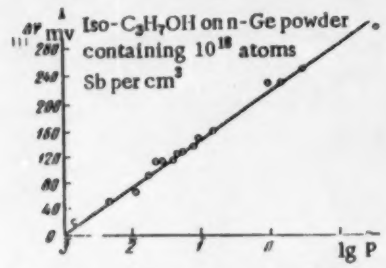


Fig. 10. Logarithmic curve for the charge, $\Delta\varphi = f(p)$ in mv during the adsorption of isopropyl alcohol on n-germanium with antimony as impurity.

$$\text{a)}\ \varphi_\theta \cong \varphi_0 \pm a \ln \bar{\theta} \text{ — (enrichment)}$$

$$\text{b)}\ \varphi_\theta \cong \varphi_0 \pm b\,\theta \text{ — (impoverishment)} \qquad (4)$$

where $\bar{\theta} = \theta/\theta_0$.

At the same time (Fig. 10), in the region where φ is essentially dependent on θ, generally:

$$\varphi_c = \varphi_0 \pm s \ln (c/c_0) = s \ln \bar{c}. \qquad (5)$$

This corresponds to the linear relationship of φ to the chemical potential of the gases undergoing sorption. The relationships (4) and (5), according to the data available in the literature, are often applied also to metals. A combination of (5) with (4a) corresponds to the Freundlich isotherm, while that of (5) with (4b) corresponds to the Frumkin-Temkin isotherm. Measurements of the charge isotherms for the mixtures are insufficiently systematic for general conclusions to be drawn. We here make the general assumption that provided the degree of saturation of the surface is not high, the effects are additive within certain limits for the adsorption of mixtures of gases whose φ values are in the same direction. The sum $\varphi_\Sigma(\theta_i)$ for enriching adsorption is given by (6a), for improverishing adsorption by (6b), and for both types by (6c):

$$\varphi_\Sigma \cong \varphi_0 \pm a \ln (\Sigma \alpha_i \theta_i/\theta_0) \cong \varphi_0 + a' \ln (\Pi \bar{\theta}_i^{s_i}), \qquad (6a)$$

$$\varphi_\Sigma \cong \varphi_0 \pm \Sigma b_i \theta_i \cong b' \Sigma \theta, \qquad (6b)$$

$$\varphi_\Sigma \cong \varphi_0 + \ln \Pi \bar{c}_i^{s_i}, \qquad (6c)$$

where α_i and b_i are coefficients not very different from unity: Π is the sign of the product. The indices α_i and s_i are positive when all the gases are electron acceptors, and negative when they are all electron donors. When simultaneous adsorption occurs of donor and acceptor gases, the picture is more complicated, but in certain cases the total value of $\Delta\varphi_\Sigma$ may probably be obtained approximately by algebraic summation of the corresponding expressions for $\Delta\varphi_a$ and $\Delta\varphi_d$ for the acceptor and donor gases. Neglecting the slight effect of V_S on k^0_{0i} and on #, we may properly replace (1) by the relationship:

$$w_i^{\pm} = n_{0i}^{\pm}\, k_{0i}^0 \exp(\Gamma E_i) f^{\pm}(\theta_{i\,\text{ads}} \cdot c_g)\, M^{\pm}, \qquad (7)$$

in which $M^{\pm} = \exp(\Gamma \Delta E^{\pm})$ is a factor denoting the modification of the charge. In the case of adsorption, $M^{\pm}$ becomes appreciable when the distance between the adsorbed charged molecules is of the order of 20A (or $N^{\pm}_{min} \cong \cong 10^{13}/cm^2$). For ordinary thicknesses of the screening zone (see Fig. 1), the charge will in such a case be weakly dependent on the distribution (ρ) of the particles with respect to E and Q, and in general the effect will lead to a shift of the corresponding distribution in the direction of lower or higher values of E (or Q), as appears in Fig. 11. In this case, for all types of particles, the corresponding values of E_i may be replaced by $E_i + \Delta E^{\pm}$, or by $E_i - \Delta E^{\pm}$, and may be used in the integral equations of the theory of processes occurring on broad, nonhomogeneous surfaces [18, 40].* In this theory, for different positions of the controlling zone, the quantity E_0 may be represented by E_{min} and E_{max} for the given surface, or some intermediate values of E which will depend on c_A, c_B, etc. [18]. In the modification factor, $\Delta E^{\pm}$ and $\Delta\varphi$ depend on the surface concentration of all the charge carriers, both ordinary adsorbed molecules and transitional complexes:

$$\Delta E^{\pm} = \Delta E(\theta^{\pm}_A, \theta^{-}_B \ldots \theta^{\#\pm}_j \theta^{\#\pm}_2 \ldots) \text{ and } \quad \Delta\varphi = \Delta\varphi(\theta^{\pm}_A \theta^{\pm}_B \ldots \theta^{\#\pm}_1) \tag{8}$$

In view of the lowness of the concentrations of all the transitional complexes, their effect on $\Delta E^{\pm}$ and on $\Delta\varphi$ may be neglected. Part of the remaining $\theta^{\pm}_j$ is due to irreversible adsorption. In the simplest case, $M^{\pm}$ in Eq. (7) may be broken down into three factors:

$$M^{\pm} \cong M^{\pm}_{\theta} \cdot M^{\pm}_{c} \cdot M^{\pm}_{R}.$$

$M^{\pm}_{\theta} \sim \exp(\pm\alpha\Delta\varphi_{\theta})$ represents the combined influence on the rate of the substances present on the catalyst surface in invariant concentration by variation in the activation energy, $\Delta E^{\pm}$.

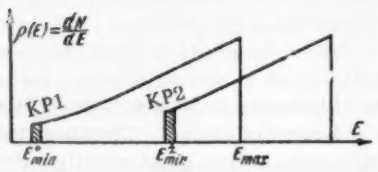


Fig. 11. The shift $\rho(E)$ in the distribution of particles of a nonhomogeneous surface in relation to E_{cat} under the influence of the charge. The controlling zone for the initial and shifted values of $\rho(E)$ is located at E_{min}.

$M^{\pm}_{c}$ is the total effect of all the substances (whether or not they participate in the transitional complex) present in mobile equilibrium with the bulk gas. These substances occupy some part of the catalyst surface, $1 - \Sigma\theta_j$, free from irreversibly adsorbed molecules. $M^{\pm}_{c} = f(c_A, c_B \ldots c_X) \sim \exp(\pm\alpha\Delta\varphi_c)$.

$M^{\pm}_{R}$ characterizes the effect of changes in the system of electron levels in the bulk of the semiconductor or the metal. Substitution of the logarithmic relationship between $\Delta\varphi$ and $\underline{c}$ given in Eqs. 5 and 6b, replace $M^{\pm}_{C}$ by the concentration factor $\bar{c}^{\pm\delta}$ and $\overline{\Pi c}_j^{\pm\delta_i}$. The fractional factor $\delta > 0$ for opposite signs of the charge of the transitional complex and c_j, while $\delta < 0$ for similar signs of charge. For additive values of $\Delta\varphi_i$ of oppositely charged forms,

$$M^{\pm}_{c} = f(c_1 c_2) \cong c^{\delta_{z_1}}_{j_1} c^{\delta_{z_2}}_{j_2} / c^{\delta_{z_1}}_{z_2} c^{\delta_{z_2}}_{z_2} \tag{9}$$

and similarly, with the concentration contribution to the kinetics on a nonhomogeneous surface. This factor is not altered in transition from w_i to Σw_i and $\int w_i$ for nonhomogeneous surfaces. It can introduce into the kinetic equations concentration factors for the products of reaction, and for substances which neither participate in the formation of the transitional complex nor are involved in any stage of the process. At the same time, the concentrations of substances participating in the transitional complex, and adsorbed with charging when $\theta > 0.01$, may enter into the kinetic equations twice, first through the function $f^{\#}(c)$, and second through $M^{\pm}_{c}$. Hence, even in the differential equations the relationship between the composition of the transitional complex and the concentration factors may vanish, and the process may present the appearance of a distorted order, and of imaginary components. Through the quantity $M^{\pm}\theta$, when a logarithmic relationship exists between $\Delta\varphi$ and θ, stepwise factors may be introduced containing $\theta^{\pm}_j{}^{\delta_i}$, and with a linear relationship between $\Delta\varphi$ and θ, the factor $\exp(\pm\beta_i\theta_j)$ may be introduced. At the same time [40], the charge may introduce a considerable change in the temperature dependence of the rates of chemisorption and catalysis, making $E^{\pm}$ into a function of T [40]. Thus, increase in T, because of the general tendency to diminution of adsorption, would cause this to be reduced, while $M^{\pm}_{c}$ and $E^{\pm}_{c}$ would vanish next, and finally $M^{\pm}\theta$ and $\Delta E^{\pm}\theta$. This may result in a change in E of 10 kcal, or even more. At sufficiently high values of the temperature, all the effects associated with adsorption modification ought to disappear. But the modifying effects of nonvolatile additives will also be weakened as the

*For microheterogeneous systems, this approximation may be too crude.

temperature is increased, since the temperature enters into the $M^{\pm}$ factor. In the simplest case, involving a single charged gas and a linear relationship between θ and φ, substitution in the corresponding isobars [18] gives, within definite limits, $E^{\pm}_T = E^{\pm}_0 \pm \lambda T$. Even with the adsorption of two substances, if these have very different values of Q_{ads}, and charges of opposite signs, at certain values of the temperature it is possible to determine experimentally the values of E. A second source of failure of the Arrhenius equation for semiconductors may be found in change in n_i with temperature. In particular, the very common change in the nature of the conductivity of semiconductors with change in temperature may result in an abrupt change in the value of E. The absolute value of ΔE in these circumstances may reach the value of ΔE_σ due to this change alone. Thus, in transition from an impurity with a low value of E_σ, or from an exhausted impurity to a true conductivity, the corresponding value of ΔE may reach $\mathcal{U}/2$. This is not usually taken into account in electronic conceptions of catalysis in which only one impurity in the semiconductor is considered, for which the component of E concerned with the generation of electrons (or holes) is inconsiderable. While semiconductor catalysts often operate under conditions when true conductivity is displayed [30, 34], where $E_\sigma \simeq \mathcal{U}/2$, they may also operate under conditions of exhausted or degenerate conductivity for which $E_\sigma \cong Q$. If the variations in $\Delta E^{\pm}$ are eliminated, and in the absence of any components introduced into $E^{\pm}$ by the electronic equilibria in the solid body, there remains a certain value of E, E_{init}, which may coincide with the height of the energy barrier of the concrete process taking place on zones of a definite type, and may include additional thermal effects introduced by the heat of adsorption.

We illustrate the general considerations set out above by means of a few examples:

The chemisorption of hydrogen on semiconductors:

$$Cat + H_2 \rightarrow Cat\begin{matrix}H\\H\end{matrix}$$

This comparatively simple process may be complicated by the dissolution of hydrogen in the preelectrode layer, and the possibility that the adsorbed hydrogen may take up both positive and negative charges. Chemisorption on metals and semiconductors, without careful preliminary purification of their surfaces from gases, usually suffers retardation according to the logarithmic kinetic isotherm [41]. Direct measurements reveal diminution of Q and increase of E with the degree of surface saturation. As early as 1941, Elley [42] noticed a sudden drop in the specific rate of isotopic exchange towards the end of the process, and expressed the view that this indicated a kinetic nonhomogeneity of the surface. During chemisorption on nonhomogeneous surfaces, not only does φ change with θ, but also the energetic state of the free zones. This is depicted in Fig. 12 by the shift of the entire distribution to right or left with simultaneous shift of the controlling zone in the direction of greater values of E. The magnitudes of these two shifts are connected between themselves by simple relationships [24]. But, according to measurements of $\Delta\varphi$, the surface charge of metals and semiconductors is not great. According to Parravano, Friederick, and Boudart [43], the absence of a kinetic isotopic effect during a direct comparison of the rates of chemisorption of hydrogen and deuterium on certain oxides points to the nonparticipation of the hydrogen in the stages which control the chemisorption, which are regarded by them as the generation of defects in the lattice. It is clear that when full use is made of the centers generated on the surface, both hydrogen and deuterium, when introduced separately, should be chemisorbed at the same rate, which should also be independent of the concentration. With chemisorption of mixtures of hydrogen and deuterium, the kinetic isotopic effect appears because of the difference in the degree of use in the active centers. For the temperature range in which the investigation was carried out, any slow electronic processes on the surface of electron transfer between the bulk of the semiconductor and the active points on its surface, seems to be more probable. The effect of the charge on the height of the barrier leads to a rate constant corresponding to $M^{\pm}_{el}$.

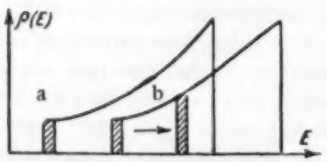


Fig. 12. Shift in $\rho(E)$ for the distribution of sections of the surface according to the value of E_{chem}, and transition of controlling zone with mean value of E under the influence of self-charging induced by adsorption. a) Controlling zone, $\theta \leq 0$, b) Controlling zone, $\theta \geq 0$.

Chemisorption is the first stage of isotopic exchange, according to the scheme:

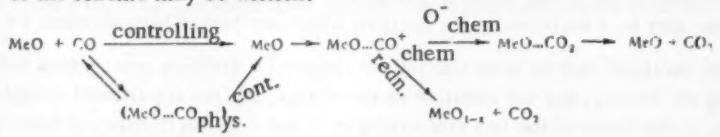
a) $H_2 + D_2 \rightarrow 2H_{ads} + 2D_{ads} \rightarrow D + HD;$

b) $H_2 + 2H_{ads} \xrightarrow{+D_2} HD + D_{ads}$

If the initial electronic processes are slow, the reverse processes ought also to be slow, and, therefore, we should expect repeated exchange to take place on the same centers until the time when they are deactivated; that is, chain processes should occur of the type by which Geib [44] in 1943 attempted to explain the high rates of exchange observed in certain cases at low temperatures.

Oxidation of carbon monoxide on oxide surfaces. The best catalysts for this process are the oxides of the transition metals. Variation in the oxygen content of the oxide catalysts from the stoichiometric quantity, or the addition of oxides of metals of different valency causes an abrupt change in the activity of the catalyst with relation to both chemisorption and activity [46]. For oxides of the type MeO, lithium and sodium oxides are particularly effective in reducing the activity. Solid solutions are formed in these cases with increased values of E_σ for zinc oxide, and reduced values for nickel oxide. According to the zone theory, this corresponds to a downward displacement of μ_{vol} (Fig. 1), accompanied by a rise in $\Delta\varphi$ (due to $\Delta\varphi_{vol}$) by an amount $\sim\Delta E_\sigma$. It is found in practice that $\Delta\varphi$ is reduced by an amount close to ΔE_σ. On the basis of Eq. (1) this would signify that $\Delta\varphi_{surf} \sim -2\Delta\varphi_{vol}$, but it has not been shown that $\Delta\varphi_{vol}$ contributes to the value of E_C. In each case this points to a positive charge of the transitional complex.

When modifying additives are present, the value of $\Delta E^{\pm}$, which enters into the value of $M^{\pm}$, is equal to $\Delta E_{cat} = \pm\alpha\Delta\varphi$, in which α is not very different from unity, and considerable compensation effect is found. The controlling stage [46, 47] is apparently the chemisorption of the carbon monoxide. This is in agreement with the positive charge of chemisorbed carbon monoxide (see Table 1) on nickel and zinc oxides. On such an assumption, either carbon monoxide in the gas phase, or physically adsorbed carbon monoxide, enters into the composition of the transitional complex; the nature of n_i is not clear, but it appears that the chemisorptive bond is formed with the participation of the d-electrons or the vacant d-orbits of Me^{n+}. Under the conditions which are being considered, the adsorptive modifiers must include oxygen, which imparts a negative charge to the surface.* One of the possible stages of the scheme may be written:



The noncoincident value of the rates of chemisorption of carbon monoxide and the associated catalytic process ($w_{chem}/w_{cat} \ll 1$) compels us to suppose as a general phenomenon in catalysis the existence of a pre-adsorption state [46]. Taking into account the increase in the negative φ-charge of the chemisorbed oxygen (Table 1) it is natural to expect a positive modifying effect ($M^{\pm}_{O_2} \gg 1$), which, apparently, is also a cause of the pre-adsorption effect [24]. It follows from this that for the widespread type of reaction, controlled by chemisorption, in which both the components in the reaction impart the same sign of charge to the surface, a reverse pre-adsorption effect ought to be found. Charges of like sign may play a considerable part in the poisoning of catalysts (for example, by water) in the reaction under discussion. If we consider the chemisorption of carbon monoxide as its dissociation on the surface: $CO \rightarrow CO^+_{ads} + \Theta$, where Θ is a surface conducting electron, it is possible to explain the first order with respect to carbon monoxide for some [47], and the $^1/_2$-th order with respect to carbon monoxide for other catalysts [49, 50]. The proposed explanation of the kinetic singularity of the reaction needs further confirmation, including work on catalysts on which the carbon monoxide is negatively charged.

Ammonia synthesis on iron catalysts. There are abundant data in support of the view that the chemisorption of nitrogen is the controlling factor in the synthesis stage, while the desorption of nitrogen controls the decomposition of the ammonia. The fact that the value of φ is reduced by promotors provides evidence that the chemisorbed nitrogen carries a negative charge. This is in harmony with the change in chemisorption in the presence

*The part played by the CO_3 complex is rendered doubtful by experiments using MnO_2 marked with O^{18} as catalyst. There is no oxygen from the catalyst in the carbon dioxide formed during the catalyzed reaction [48].

of promotors (Table 1). This assumption would lead us to expect negative modification by substances which become negatively charged on adsorption. It is probable that certain contact poisons operate in this way. It is characteristic of the ammonia synthesis that the process is reversible, and that a state of partial equilibrium is maintained between the chemisorbed nitrogen and the ammonia and hydrogen during the course of the reaction [18]. In the reverse process, the transition from N_2^- to the transitional complex $N_2^{\#-}$ occurs without change in the sign of the charge, and it might appear that the rate of desorption of nitrogen does not include $M^{\pm}$. This is not actually the case, since $f^{\#}$ includes N_2 ads [or $(N^-_{ads})^2$], connected by the equilibria: N_2^- ads $\rightleftharpoons N_2^{\#-}$ ads, and N_2^- ads + $3H_2 \rightleftharpoons 2NH_3$. When this is taken into account, the equations for the direct and reverse reactions take the form:

$$\vec{w}_i = \vec{k}_0 \exp(\vec{\Gamma} E_i) f_{N_2^-} M^{\pm} = \vec{k}_0 \exp|\Gamma (E_i + \alpha \Delta\varphi_{K,O})| \; M^{\pm}_{\theta,c}(N_2); \qquad (10a)$$

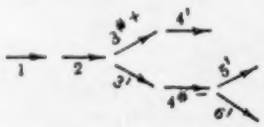
$$\vec{w}_i = \vec{k}_0 \exp(\overleftarrow{\Gamma} E_i) f_{N_2^-} M^{\pm} = \vec{k}_0 \exp|\Gamma (E_i + \alpha \Delta\varphi_{K,O})| \; M_{\theta,c}(NH_3)^2/(H_2)^3, \qquad (10b)$$

in which the arrows denote the direction of the reaction; $\overleftarrow{E}_i = \vec{E}_i + Q$; Q is the heat of the ammonia synthesis. Equations (10a) and (10b) differ from the initial equations of Temkin and Pyzhov [51] in the same way for both the forward and the reverse reactions, and in general this is true for all the terms of the factor $M^{\pm}$. For equal degrees of surface nonhomogeneity [18], and with $\rho(E_i)$ and $\rho(Q)$ constant, the Temkin kinetic equation follows from this.

Effect of charge on complex reactions. The results which have been stated are inadequate for the analysis of complex, multistage processes which give a mixture of substances which may contain the end-products of a single, branched process, or of independent parallel processes, together with the most stable intermediate products. For the independent parallel processes, which may take place on the same active centers as the main process or on different ones, the main possibilities for two parallel directions are shown in Table 4.

For difference in charge between the transitional complexes (e.g., for $\#_1^+$ and $\#_2^0$, or for $\#_1^-$ and $\#_2^+$), the relationships are well-defined. For the same sign of the charges of the two transitional complexes, the selectivity may be either constant or variable. Figure 13 gives the changes in distribution with respect to E_1 and E_2 for certain combinations of charge signs. Owing to the presence of optimum values of Q_{ads} and E under the influence of V_S, there may also occur a shift of the position of the controlling zone for reactions with transitional complexes of different signs; that is, a variation in the sections which are basically responsible for the process.

The results obtained may be used also for the stages of a dividing process (see Scheme 1). If the stages 1 and 2, preceding the forking, are not sensitive to the charge, but the transitional complex is the controlling stage, even though one of the limbs of the fork (for example, 3 and 4 in the illustration below) is charged, the relationship given in Table 4 for w_1, w_2 and w_1/w_2 will be completely applicable:



In determining the neutral stage 1 or 2, prior to the forking, the charge, while changing the selectivity, will have but little effect on the rate. This is presumably the reason for the effect of nonmetals introduced on to silver catalysts during the oxidation of ethylene into ethylene oxide, which reduce the extent of the oxidation to carbon dioxide by favoring the parallel reaction, while leaving almost unaffected the formation of carbon dioxide in the subsequent process. Other relationships are found in the modification of oxide catalysts for the oxidation of propylene into acrolein [29].

In the sequence of stages of a complex reaction, there may take place alternatively reactions between the individual adsorbed molecules, the individual gaseous molecules, or adsorbed and gaseous molecules together. The stages may be differentiated according to the type of process and according to the number of active centers taking part in them. If we wish to understand the influence exerted by the charge, it is essential that when the surface is positively (or negatively) charged, at one of the initial stages there shall be present subsequent stages with electronic transfer occurring in the opposite sense, since the gas supplies (or accepts) only neutral molecules.

TABLE 4

Effect of Increase in V_S on the Rates of the Parallel Reactions, $\vec{w}_1$ and $\vec{w}_2$, and on their Ratio (selectivity)

Charge #1	w	Charge #2: +	Charge #2: 0	Charge #2: −
+	w_1 w_2 w_1/w_2	increases increases constant or diminishes	increases constant increases	increases diminishes increases greatly
0	w_1 w_2 w_1, w_2	constant increases diminishes	constant constant constant or diminishes	constant diminishes increases
−	w_1 w_2 w_1/w_2	diminishes increases diminishes greatly	diminishes constant diminishes	diminishes diminishes constant or diminishes

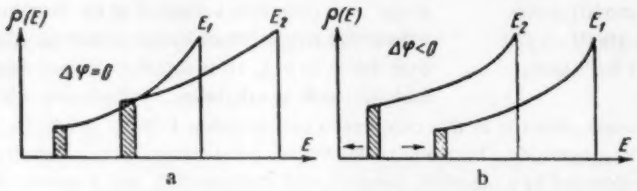


Fig. 13. Initial distributions for two nonidentical stages. a) $\rho(E_1)$ and $\rho(E_2)$; b) the same after mixing associated with charge effects.

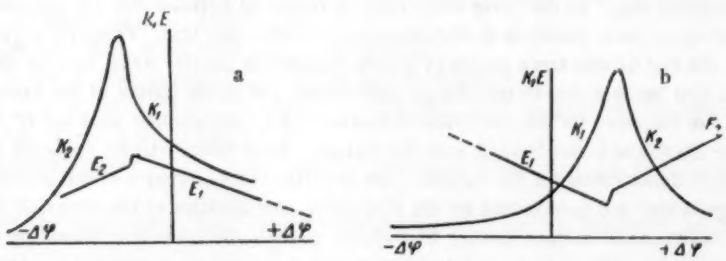


Fig. 14. Schematic curves for the modification of charge with displacement of the controlling stages: a) when $\Gamma < 0$; b) when $\Gamma > 0$.

As a particular example, in the catalytic oxidation of carbon monoxide, the initial transfer of negative electrons to the catalyst from the carbon monoxide takes place with the formation of CO_{ads}^{+}, and therefore, in one of the subsequent stages, such as the transition into carbon dioxide or the desorption of carbon dioxide, neutral molecules must arise through a transfer of electrons in the opposite direction. Since all the factors which tend to modify the surface charge operate in opposite senses on any processes accompanied by positive or negative charging of the surface, the influence of additives and adsorbed substances which change the value of φ of the surface ought to accelerate certain stages of the reaction and retard others. In the initial control of the stages which are accelerated by additives when $\Gamma < 0$, E should diminish with increased charge, and $w_{contr} = w_1$ should increase. The activation energies of all the stages with the opposite direction for electronic transfer should in

this case increase with increase in V_S (see Fig. 14a, right-hand side). For sufficiently large values of $\Delta\varphi$, this should lead inevitably to a displacement of the stages after the attainment of some optimum value of E, E_{opt}, which will be equal to, or close to, E_{min}. When there is initial increase in the value of E of the controlling stage and diminution of $\underline{k}$ when additives are introduced, there is no basis for any shift of the controlling stage. In the temperature range for which $\Gamma > 0$, the changes in w_1 are in step with those in E_1. Because of this, any maximum for $\underline{w}$ corresponding to a minimum value of E ought to be excluded, but the left-hand portion of Fig. 14b reveals maxima for E and $\underline{w}$ for closely similar values of $\Delta\varphi$.

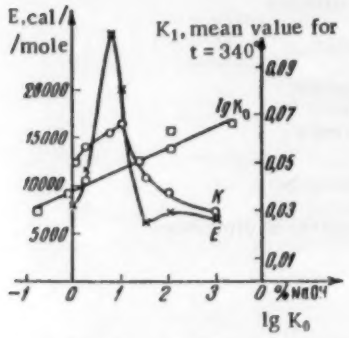


Fig. 15. Effect of the modification of tungsten trioxide by alkali on the exhaustive oxidation of isooctane.

A range of data obtained for modified oxide and metallic catalysts [20] is in accordance with the scheme just presented, apart from the trace of a minimum found in the work of L. Ya. Margolis and O. M. Todes [52, 20]. This suggests that shift of the controlling stages occurs towards the point of maximum $\underline{w}$, which had been postulated by us in 1940 [20], takes place, and supports the explanation of such maxima given by Hauffe [53] and by Schwab [31], on the basis of the assumptions of the limiting layer theory. We note, however, that measurements of $\Delta\varphi$ for metal films promoted by gases [54], suggests that it may also be possible for a maximum to arise through a change in the sign of $d\varphi/d\theta$ owing to a change in the position of the promotor above some optimum value of θ (θ_{opt}).

We may cite as characteristic examples of the process taking place with optimum values of $\underline{w}$ for maximum values of E, the exhaustive oxidation of hydrocarbons on oxide catalysts. The relationship shown in Fig. 15 is found even for comparatively simple hydrocarbons (such as ethylene). In harmony with the conclusions arrived at above, the compensation effect is in this case very considerable: $\Gamma > 1$ and k_0 for comparable samples may vary by several orders of magnitude. Possible explanations of the compensation effect, which were first given in the work on catalysis published by Constable, Schwab, and Cremer [27], are a matter of great interest, and have recently been analyzed [55, 56].

The examples which have been analyzed with respect to the effect of charge relate to the oxidation-reduction class of reactions, taking place on metal and oxide catalysts. For such reactions the value of φ may exert a direct influence on the elementary catalytic act. However, there should be an effect due to the charge in acid-base reactions also,* in the cases when there is reason to believe that the formation of labile, intermediate charged forms takes place, as in the example of carbonium ions. Thus, for a given degree of charge, the reactions of the two named large groups [57] may proceed in similar ways, and the differences between them upon actual catalysts are due, not to the charge differences, but to the nature of the intermediate particles (whether positive or negative for the oxidation-reduction class, and whether we have H^+ or H^- for the acid-base class), and to the chemical bonds formed with the surface. Such bonds will be covalent bonds for the former class, and acceptor-donor bonds for the second. The specific characteristics of the primary catalytic acts, and the selection regularities are determined by the electronic peculiarities of the chemical bonds, and the chemical structure of the intermediate surface forms. The latter, in their turn, are determined by the electronic peculiarities of the atoms on the surface of the solid material and in the reacting molecules. Measurements of the integral electrical properties of the system are not very helpful in such a case, and the measurement of magnetic properties is considerably more to the point [58], particularly electronic paramagnetic resonance and infrared spectroscopy [58, 59]. The latter especially has revealed the existence of real differences in the nature of the changes in molecules under interaction with oxidation-reduction and acid-base catalysts, and has also shown the biographical nonhomogeneity of a number of surfaces [58]. The comparatively few quantum-mechanical calculations of the energy of chemisorption-bonds, principally carried out in the works of Eyring and Millikan, give reasonable orders of magnitude, but they are relevant only to the rupture and formation of σ and acceptor-donor bonds. Meanwhile, the selection rules and the singularity of the elementary activating act cannot be understood without assumptions concerning the nature of the bonds which have no strict classical analogy. For example, we must take into account π-bonds for the adsorption of unsaturated and aromatic compounds, hydrogen bonds,

*But not on organic cationites and anionites.

dative bonds, and various complexes with multicentered orbitals, and electron defects, which are so widespread in the chemistry of complex compounds [60]. It is through the participation of such bonds, apparently, in the first instance, that intermediate endothermic forms are formed, the energy absorbed on formation being E. These can also account for the peculiarities of the orientation of the molecules on the surface, and a number of special laws of catalysis. A more detailed discussion of this aspect of catalysis will be presented in another place. We limit ourselves here to the observation that in electronic theories of catalysis it is usual to over-estimate the part played by integral electronic properties of a remote-acting kind, and to underestimate the significance of specific short-distance electronic-chemical interaction of the atoms which constitute the surface of the catalyst with the molecule of reagents, and also of the collectivization of electrons into complex many-centered complexes, formed between the atoms of the surface of the solid body and the molecules of the reagents.

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THE MAIN CONCEPTS IN THE ELECTRONIC THEORY OF CATALYSIS ON SEMICONDUCTORS*

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A brief outline is given of the modern theory of catalysis on semiconductors, with emphasis on the aspects that have formed the special province of the author and his colleagues. The main results are summarized, and some consequences of these results are indicated. The mathematical side of the theory is not presented. The main results relate to: a) chemisorption involving charged and neutral forms, b) radical and saturated-valence forms of chemisorption, c) transitions between the various forms of chemisorption, d) equilibrium between the various forms of chemisorption, e) adsorptivity of a surface, f) catalytic activity of a surface, and g) role of the Fermi level. Some consequences concern: a) the effects of chemisorption on the electrical conductivity and work function, b) relation between surface and bulk effects, c) correlation between electrical conductivity and catalytic activity, d) effects of impurities on the catalytic activity, and e) effects of illumination on the adsorptivity.

Introduction

The objects of the electronic theory of catalysis are two, since:

1. Any heterogeneous catalyzed reaction, as in fact any chemical reaction, has an electronic mechanism. One object of the theory is to reveal the mechanism, which must be understood if we are to control the effect. Catalysis cannot be other than a crudely empirical subject until the detailed mechanism of any catalyzed reaction is understood.

2. It is clear that the catalytic behavior of a semiconductor is very closely related to electronic processes occurring within and upon that material. The electronic parameters of a semiconductor show a definite correlation with the catalytic activity. The second object of the theory is to determine that correlation; the two objects are, naturally, very closely connected.

L. V. Pisarzhevskii may be considered as the originator of the electronic theory of catalysis; in 1916 he attempted to relate the catalytic behavior of a solid with the solid's electronic parameters. Naturally enough, Pisarzhevskii's theory did not go beyond Bohr's, which meant that it was somewhat limited in its application. The theory is at present developing rapidly throughout the world; the main Soviet workers include Roginskii (whose laboratory has been the source of many papers on this topic), Terenin, Lyashenko, Myasnikov, Keier, and so on. My colleagues and I have done a great deal of theoretical work on this topic. Outstanding foreign workers in this field are Bowden, Egren, Boudart, Weiz and (especially in recent years) Hauffe and his school, who have made a great contribution to the theory.

*Paper presented at the Second International Congress on Catalysis.

The aspect that I have been concerned with is the quantum-mechanical treatment of the interaction between a molecule and the lattice of a solid. That treatment was begun with very simple models and then was extended to more complicated cases; the results so obtained gave rise to several deductions. I present here very briefly the main results and the deductions that derive from them. The mathematical aspect of the treatment is omitted; those interested in this aspect should refer to the original papers. Again, I have omitted (due to lack of space) the numerous experimental results that have been interpreted. A more detailed survey of the theory is to be found in my article in Volume 12 of "Advances in Catalysis."

I. The Main Results

a) Chemisorption of Charged and Neutral Forms

Particles adsorbed on a crystal are treated in the theory as a special type of defect (as local flaws in the strictly periodic structure of the surface). They are impurities introduced into the surface, to use the terminology of semiconductor physics.

I first used this approach in 1948 [1], when I represented the lattice and a chemisorbed particle as a single quantum-mechanical system; in this way the particle was included automatically in the electronic behavior of the lattice.

In this treatment, a chemisorbed particle acts as a localization center for free electrons and holes. Such particles may behave as donors and as acceptors; in some cases both types of behavior occur together. (Acceptor-donor defects of this kind are well known in the physics of solids.)

On this basis we may differentiate the electrically neutral form of chemisorption (free electrons and holes are not involved) from chemisorption in the form in which the chemisorbed particles trap electrons or holes.

There are two points to be noted here:

1. A free electron or hole localized on or near a chemisorbed particle takes part in the chemisorption bonding. The electron or hole affects the type of bond formed between the particle and the lattice; the results is always (see [2, 4]) that the bond is strengthened.

The bonds produced in the neutral form we may call weak, and those in the other form strong. These terms are only relative, of course, for there are in fact two types of strong bond. A bond involving a free electron we shall call an n-type bond (acceptor bond), whereas one involving a hole we shall call a p-type bond (donor bond).

2. These two types of strong bond can be purely ionic, purely homopolar, or (the general case) mixed. The nature of the bond is governed by the character of the localization (i.e., by the natures of the impurity and of the adsorbent), and so is dependent on the way in which the electron (hole) is distributed between the adsorbed particle and the adsorption center [5-6].

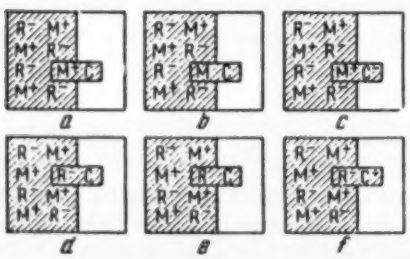

Fig. 1.

Figure 1 illustrates the various types of bond for some particles C adsorbed in an ionic crystal MR whose ions are M^+ and R^-. A free electron in such a crystal corresponds to a neutral state M, which moves from one M^+ ion to another; again, a hole corresponds in general to a neutral state R, which moves in a similar fashion. Weak bonds are shown in Fig. 1a and d; strong acceptor bonds in Fig. 1b and c; and strong donor bonds in Fig. 1e and f. Parts b and e correspond to purely homopolar bonds, and parts c and f to purely ionic bonds (the real situation is usually somewhat intermediate).

The first result from the theory is this scheme of bond types and charges. The various types of bond are related to the capacity of the adsorbed material to form bonds to electrons or holes, or (which is the same) to the capacity to donate electrons or holes to the lattice.

b) Radical and Saturated-Valence Forms of Chemisorption

The various types enumerated above can be divided further in accordance with the chemical form taken up y the particle, which may be a normal molecule, a radical, or an ion radical.

Radicals and ion radicals are produced by the free carriers, which act (see [2, 7-9]) as free surface valencies (electrons, positive valencies; holes, negative valencies).

The weak form is one in which free surface valencies are not involved; the strong form, one in which they are. The adsorption is of acceptor or donor type in accordance with the type of surface free valency used (positive or negative). This interaction with the free valencies causes a neutral molecule to be transformed to an ion radical, whereas a radical is transformed to a molecule bearing a charge.

Figures 2 and 3 illustrate this situation (in terms of symbolic valence lines) for Cl and CO_2, respectively.

Figure 2a shows a weak bond to a Cl atom (radical chemisorption); the free valency of the Cl atom remains unsatisfied. A strong bond (acceptor or donor, Fig. 2b or 2c) corresponds to use of that valency by a positive or negative free valency in the surface.

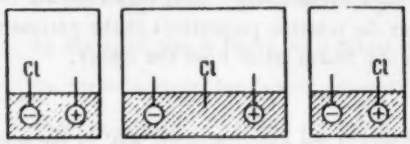

Fig. 2.

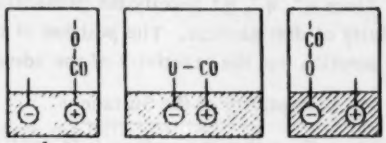

Fig. 3.

Figure 3a shows a CO_2 molecule held in weak chemisorption by two valence bonds. Here we have adsorption at a virtual Mott exciton, i.e., at an exciton generated by the act of adsorption. The valencies are satisfied; the adsorbed particle is electrically neutral. Figures 3b and 3c correspond respectively to strong donor and strong acceptor types. Ion radicals are present in both cases.

The adsorbed particle is more reactive in the radical types of adsorption; it is more ready to react with some other particle in the gas or adsorbed on the surface. We see that the various types of chemisorption differ not only in bond strength and in sign of charge, but also in the reactivity of the adsorbed material. This is the second result from the theory.

c) Transitions Between the Various Types of Chemisorption

The third result from the theory is that the various types of chemisorption can be transformed one into another; a chemisorbed particle remains adsorbed but changes the type of bond formed to the surface. These changes are associated with localization or delocalization of the free electron or hole present on or near the particle.

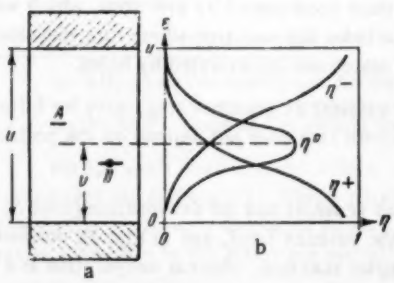

Fig. 4.

These changes may be represented in terms of the band scheme for the semiconductor (Fig. 4a). The particle is represented as a donor level D and an acceptor level A; transitions can occur between these levels and the bands as a result of thermal agitation (the temperature must not be too low in the case of a semiconductor). The result may be that an electron is trapped at A or is lost from D.

The trapping of an electron at A means that the bond has ceased to be weak and has become a strong acceptor bond; the electron may come from the conduction band or from the valence band. Again, the loss from D means that the bond has become a strong donor one; the electron may have combined with a free hole in the valence band or may have passed to the conduction band [3, 4, 8, 10].

Thus, a weak bond may become strong either as a result of the loss of a surface free valency (a free electron or hole becomes localized), or without such loss; in the latter case, a valence bond within the lattice is broken, and a surface free valency is generated (a free electron or hole is produced).

We see that the role of electrons and holes in chemisorption can be described in terms of the band theory of solids, which deals with the energy aspects of chemisorption.

d) Equilibrium Between the Various Forms of Chemisorption

Electronic equilibrium is reached almost instantly in a semiconductor, so there is a definite probability of finding a chemisorbed particle in a given state. Of the total number of particles adsorbed on unit surface, a fraction η^0, will be weakly bound, a fraction η^- will be bound by strong acceptor bonds, and a fraction η^+ will be bound by strong donor bonds. These quantities denote the proportions of the various forms; they also indicate the mean lifetime of a particle in these states.

It may be shown [6, 11] that η^0, η^-, η^+ are determined by the position the Fermi level takes at the surface, other things being equal. The relation of η^0, η^-, η^+ to that position ϵ is shown in Fig. 4b; we see that η^- increases and η^+ decreases as the level rises from the top of the valence band, whereas η^0 has a maximum. Almost all of the particles act as donors if the level is low; and almost all act as acceptors if it is high.

Since η^0, η^-, η^+ specify the probabilities that a particle is the corresponding states, they indicate the reactivity of that particle. The position of the Fermi level controls the relative proportions of the various types of chemisorption and the reactivity of the adsorbed material. This is the fourth result from the theory.

e) Adsorptivity of the Surface

We assume that the surface is in equilibrium with the gas phase; if the electron-hole 'gas' in the semiconductor is not degenerate, the equilibrium with the gas phase is maintained solely via weak chemisorption [12]. Only those particles that are bound by weak bonds are lost to the gas phase; the strongly bound ones do not exchange directly with the gas.

This implies that the adsorption capacity for a given compound at a given temperature and pressure (i.e., the total number of molecules bound per unit area) is controlled by η^0, that is, by the position of the Fermi level. The capacity varies as that level moves, other factors remaining unchanged. This is the fifth result from the theory.

The strong form of chemisorption results in the surface of the semiconductor becoming charged when a compound is adsorbed, because the molecules bind electrons or holes on or near themselves. The magnitude and sign of the charge depend on the number and nature of the adsorbed molecules and on the position of the Fermi level for the system as a whole [11]. The charge may be nearly zero if donor and acceptor bonds occur in roughly equal numbers, or if the weak form is the main type of chemisorption.

f) Catalytic Activity of a Surface

The rate of the reaction at the surface depends on the reactivity of the particles; here η^0, η^-, η^+ and the position of the Fermi level appear in the final expression for the reaction rate. The rate depends on the position of the Fermi level. This is the sixth result from the theory.

All heterogeneous reactions can be divided into two broad classes in accordance with the way the rate is controlled by the position of the Fermi level. The first class includes any reaction whose rate increases as the Fermi level rises (other things being equal). This is the class of reactions accelerated by electrons, which we may call acceptor reactions or n-type reactions. The second class includes any reaction whose rate increases as the Fermi level falls; this is the class of donor or p-type reactions,which are accelerated by holes.

The various stages of a reaction sequence may fall in different classes; an acceptor stage may be followed by a donor stage and so on. Again, it is possible to have a reaction whose rate does not depend on the position of the Fermi level.

Figure 5 shows the rate g as a function of ϵ for dehydrogenation (case a) and for dehydration (case b) of an alcohol [13]. In Fig. 5a we calculate ϵ upwards from the top of the valence band, and in Fig. 5b downwards from the bottom of the conduction band. Dehydrogenation is an acceptor reaction, whereas dehydration is a donor reaction. The first is retarded and the second is accelerated when the Fermi level falls. The selectivity of the catalyst can be controlled in this way. Factors that tend to depress the level will tend to suppress dehydrogenation and to promote dehydration, and vice versa.

Figure 6 shows the rate g as a function of ϵ for the oxidation of CO. The reaction accelerates, reaches a maximum at M, and then slows down as the Fermi level is raised. The reaction is of the acceptor type in the region AM, but becomes of the donor type in region MB. The position of M depends on the conditions, i.e., on the partial pressures of the components and on the temperature. The curve AMB changes in shape and position as the conditions vary. We may pass from branch AM to branch MB or conversely if we substitute one specimen for another made in a different way or if we vary the conditions.

g) Role of the Fermi Level

We have seen above that the position of the Fermi level at the surface determines all the main chemisorption and catalysis parameters. The position of the Fermi level controls:

1) the balance between the various forms of chemisorption (between the various types of bond to the surface),

2) the reactivity of the chemisorbed material (the probability of finding the compound in radical or molecular form),

3) the capacity of the surface (the number of particles per unit area at equilibrium at a given temperature and pressure),

4) the magnitude and sign of the charge for a given degree of saturation,

5) the catalytic activity for a given reaction, and

6) the selectivity for two (or several) concurrent reactions.

The Fermi level is clearly the factor controlling chemisorption and catalysis. It is the key to the control of activity and selectivity, other things being equal. I dealt with this role of the Fermi level in one of the earliest papers on the electronic theory of catalysis [13]. Subsequently Boudart [14], and more recently Hauffe [15], have considered the topic.

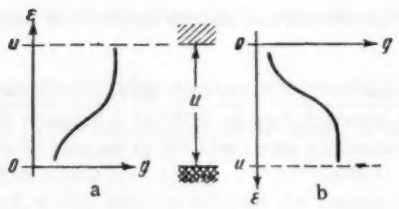

Fig. 5.

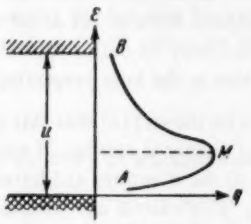

Fig. 6.

The position of the Fermi level controls the electron and hole concentrations at the surface. This points to the physical significance of the Fermi level in chemisorption and catalysis; it also demonstrates the characteristic correlation between the adsorptivity and catalytic activity on the one hand and the free-carrier concentrations on the other.

II. Some Consequences

a) Effects of Chemisorption on the Electrical Conductivity and Work Function

I give below some of the consequences deriving from the above results.

First, I shall deal with the effects caused by the charge on the surface. The charge causes the bands to be curved near the surface [11]; Fig. 7 illustrates this (negative charge Fig. 7a, positive Fig. 7b, neutral Fig. 7c). The results is that ϵ is displaced by an amount $\Delta\epsilon$ relative to its position ϵ_0 within the crystal. The zone curvature gives rise to the following two effects.

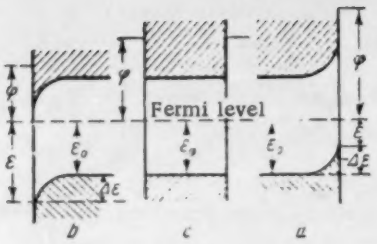

Fig. 7.

The first is that the electrical conductivity is affected; the position of the Fermi level controls the electron concentration in the conduction band and the hole concentration in the valence band. The curvatures shown in Figs. 7a and 7b result in the electron and hole concentrations varying from point to point in the semiconductor. The electrical conductivity of the surface layer is thereby affected, and the conductivity of the whole crystal may be appreciably affected if the crystal is small.

The second is that the work function is altered. (The work function is denoted by φ in Fig. 7). The work function is by definition the distance (in energy terms) from the Fermi level to the free space outside the crystal. A negative charge increases the work function, whereas a positive one decreases it, as we may see by comparing parts a, b, and c of Fig. 7 (if we neglect the additional step in the potential occurring at the double layer produced by adsorption).

The two effects have been examined in detail as regards theory and experiment by a number of workers here and abroad.

b) Relation Between Surface and Volume

The $\Delta\epsilon$ of Fig. 7 clearly varies with the degree of saturation of the surface, i.e., is a function of the pressure P. It varies with ϵ_0 if P is fixed, so ϵ is controlled by ϵ_0 at any fixed pressure. This demonstrates that the surface properties (which depend on ϵ) are related to the bulk properties (which depend on ϵ_0). This correlation is the second consequence of the theory [16].

A point here (which can be demonstrated in general) is that any shift in the Fermi level within the crystal (upwards or downwards in Fig. 7) results in a similar shift in the Fermi level at the surface. This indicates how we must alter the bulk properties in order to produce specified surface properties.

Further, in one particular case (which is of independent interest) the position of the Fermi level at the surface may depend little or not at all on the position within the crystal. In this case the bulk has no effect on the surface, which may be called quasiinsulated. Here ϵ and ϵ_0 are not correlated, and the behavior of the surface is not sensitive to the bulk properties.

It can be shown [16] that this case occurs when the semiconductor has a fairly high density of surface states (e.g., has an adequate number of surface defects of various kinds), provided that the difference between the concentrations of the electrons and holes localized at the surface is reasonably small relative to the sum of those concentrations. This case is encountered frequently.

c) Correlation Between the Catalytic Activity and the Electrical Conductivity

The correlation between the catalytic activity and the electrical conductivity is an example of the connection between surface and bulk properties. Different specimens of the same material made in a different way will differ in conductivity, and so should differ in catalytic activity. The two properties may increase together, or the latter may fall as the former rises; the class (n- or p-) of the reaction is decisive here, as is the nature (n- or p-type) of the semiconductor.

The electrical conductivity is controlled by ϵ_0 (Fig. 7) and (if the crystals are very small) by $\Delta\epsilon$ as well, whereas the catalytic activity is controlled by ϵ, which itself depends on ϵ_0, other things being equal. Any rise or fall in ϵ_0 is accompanied by a rise or fall in ϵ.

Thus, any factor that displaces the Fermi level within the conductor (that alters the electrical conductivity) will also displace that level at the surface (will alter the catalytic activity). Any factor that affects only the latter level (that affects only the curvature of the bands) will also affect the electrical conductivity and the catalytic activity.

Any change in the conductivity is accompanied by a change in the catalytic activity, in general; I predicted this as long ago as 1950 [13, 17] on a theoretical basis, although at that time there were no experimental

results available to test that prediction. Now there are many papers on the subject, in which that prediction has been confirmed; the electrical conductivity and catalytic activity have been measured on specimens differing in mode and preparation, and it has been found that changes in the one parameter are accompanied by changes in the other.

A correlation between the two parameters is not observed in every case, because the reaction rate may not depend on ϵ over certain ranges in ϵ. This situation can occur with a semiconductor having a quasiinsulated surface, for which ϵ does not depend on ϵ_0 (if the crystals are not too small).

d) Effects of Impurities on the Catalytic Activity

Now I turn to the effects of impurities on the activity and selectivity of a catalyst, these effects being consequences of the theory [1, 13, 17].

An impurity on the surface of or within a crystal can alter the position of the Fermi level at the surface. This effect on the Fermi level is responsible for the effect on the catalytic activity of the surface at a given degree of saturation. This indicates how traces of impurities can promote or retard a reaction even though they do not come directly in contact with the reactants. Thus the effect on the catalytic activity and the parallel changes in that activity and in the conductivity are two different consequences of the same basic mechanism.

Any acceptor impurity tends to move the Fermi level downwards; any donor, upwards. This means that an acceptor impurity retards acceptor reactions (poisoning), whereas a donor impurity accelerates them (promotion). The situation is reversed, of course, for donor reactions.

A reaction having two stages, one a donor and the other an acceptor, can show a transfer from one stage as the rate-limiting step to the other as the Fermi level changes in position. Figure 6 shows $\underline{g}$ as a function of ϵ for a reaction of this type; impurity incorporated into the crystal may cause a transfer from the lower branch of the curve AMB to the upper branch, or vice versa. Thus an impurity that acts as a promoter at one concentration may act as a poison at another.

If there are two parallel reactions possible, one an acceptor and the other a donor, then one will be favored and the other will be retarded as the Fermi level moves in one direction, and conversely when the level moves in the other direction (e.g., as in Fig. 5a and $\underline{b}$). The impurity alters the balance between the two reactions, and so may be used to adjust the activity and selectivity of the catalyst via its effect on the Fermi level.

e) Effects of Illumination on the Adsorptivity

A further consequence of the theory is that light affects the adsorption capacity of a semiconductor.

The electron and hole concentrations at the surface are altered when photoelectrically active light is absorbed, so the balance between the various forms of chemisorption is also affected. Then η^0, η^-, η^+ will have one set of values for an illuminated crystal and another set of values for a crystal in the dark. Light that produces free electrons increases the proportion of the strong acceptor form and decreases the proportion of the donor form; light that produces holes has the reverse effect. The proportion of the neutral form is controlled by the gas pressure and is not affected, in general, by the presence or absence of light. The general effect of illumination is thus to alter the proportions of the strongly bound forms (i.e., the adsorptivity) at a given temperature and pressure.

The uptake may be increased by the light (photoadsorption), may be reduced (photodesorption), or may be unaffected (inactive absorption). It can be shown [12] that the effect is controlled by the relative changes in the electron and hole concentrations. Photoadsorption and photodesorption have been demonstrated by experiment.

It may also be shown [12] that the effect is controlled by the history of the material (i.e., by the position of the Fermi level) as well as by the illumination conditions and by the natures of the adsorbent and of the adsorbed compound. Enrichment in a donor impurity will raise the Fermi level, in which case photoadsorption may give way to photodesorption, conditions otherwise remaining unchanged. An acceptor impurity naturally has the reverse effect.

SUMMARY

I have dealt above with the basic results from the theory and with some consequences. Many other consequences might be quoted. Here I summarize in a few lines the theory at its present stage of development.

It has been shown that free electrons and holes take part in forming chemisorption bonds; they act as free valencies, and their presence is responsible for the strength of the bonds and for the reactivity of the chemisorbed material. The consequence of this is that all the formulas contain the Fermi level, which itself has other consequences. The Fermi level connects the catalytic and adsorption parameters of the surface with the state of the crystal as a whole. The consequences of this connection are dealt with by the theory.

The theory can be presented in three different forms, namely:1) in terms of simple models such as that shown in Fig. 1; this form is convenient for describing the geometrical aspects, 2) in terms of valence bonds; this form is best suitable to discussions of chemical features (examples are Figs. 2 and 3), and 3) in terms of a rigorous description of the energy bands, which enables us to consider the detailed mechanism. Figures 4a and 7 give examples; any given problem can be represented in any of these three forms, in general.

Two remarks may be made in concluding.

Firstly, the theory is at present far from complete in its development; it resembles a building under construction, in which the scaffolding has not yet been removed.

Secondly, the theory is not in competition with other theories of catalysis, because its approach is entirely different; its object is to reveal the microscopic mechanism, and its treatment is controlled by that object. The phenomenological theory of catalysis stands in relation to the electronic theory roughly as the theory of the chemical bond current in the last century (valence lines being the sole tool) stands in relation to the modern quantum-mechanical theory; the last of these has given the valence lines a physical meaning and has revealed the physical nature of chemical bonds.

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THE USE OF ELECTRON PARAMAGNETIC RESONANCE IN CHEMISTRY

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The principles of the method of electron paramagnetic resonance (EPR) are described. A review is given of the results obtained in the author's laboratory by the use of EPR for the investigation of the structure of paramagnetic particles – aromatic negative ion-radicals formed by the action of ionizing radiation on polymers. The results of a quantitative investigation of the direction and rates of conversion of certain radicals in the solid phase are given.

1. Introduction, Principles of the Method

The phenomenon of electron paramagnetic resonance (EPR), discovered in 1944 by E. K. Zavoiskii [1], consists in the fact that the paramagnetic particles present in a constant magnetic field H can absorb the energy of a high-frequency field if these fields are perpendicular to each other and if the condition

$$h\omega = g\mu_B H, \tag{1}$$

where ω is the frequency of the high-frequency field; μ_B is Bohr magnetons and g is the spectroscopic splitting factor, coinciding in the case of free atoms with the Lande factor, is satisfied.

Simply the occurrence or absence of the EPR spectrum in an investigated sample can give a chemist very valuable information. In actual fact, from an investigation of a chemical process on this basis, conclusions can be drawn regarding the radical or ion-radical mechanism; in an investigation of the structure of highly involved complexes or solid bodies containing heavy atoms with unpaired electrons in the inner shells, the absence of an EPR signal can serve as an indication of the characteristics of the electronic structure of these atoms. The use of the EPR method made it possible to detect unpaired electrons in complex organic compounds with conjugated bonds, in which thermal excitation to the triplet state can evidently already take place at fairly low temperatures [2]. On the other hand, the EPR method has made it possible to discover appreciable paramagnetism in complex conjugated systems [3, 4], even without their excitation to the triplet state. Radicals were discovered by the action of ionizing radiation on solid bodies and frozen liquids [5]. By means of this method, it was possible to make quantitative measurements of the diffusion of free radicals and the kinetics of elementary acts of chemical change involving the participation of radicals in the liquid [6] and solid phase [7] and investigate free radicals formed during fermenting processes [8].

One of the most important characteristics of the EPR absorption signal is its position in the field, determined by the value g in Eq. (1) (g factor). On the basis of the g factor, it is frequently possible to draw specific conclusions regarding the localization of an unpaired electron in an investigated paramagnetic particle and the character of the bonds.

Another method of approach to an investigation of the properties of a paramagnetic particle is the analysis of the form of the EPR signal. For symmetrical lines the form is determined by the type of functional relation

between the intensity of absorption and the frequency or the magnetic field strength [I = $f(\omega)$ or $f(H)$] and the sole parameter included in this relation. The width of the line at the half-height ("half-width") or the distance between the points of maximum slope are generally selected as such a parameter. In the absence of exchange reactions or translation effects, associated with rapid migration of unpaired electrons in the structure, the form of the line is described by Gauss's Law:

$$I = I_0 \exp\left(-\frac{\Delta\omega^2}{\overline{\Delta\omega^2}_{og}}\right), \tag{2}$$

where $\Delta\omega$ is the distance from the center of the line, and $\Delta\omega_{og}$ is a half of the half-width. In the presence of exchange reaction or translation effects with a frequency ω_e greater than the half-width of the line, the main part of the signal is described by Lorenz's formula:

$$I = I_0\left(1 + \frac{\Delta\omega^2}{\overline{\Delta\omega^2}_{ol}}\right)^{-1}, \tag{3}$$

where $\Delta\omega_{ol}$ has the same significance as $\Delta\omega_{og}$ in Eq. (2).

It has been shown by van Vleck [9] that

$$\overline{\Delta\omega}_{ol} \approx \overline{\Delta\omega}^2_{og}/\omega_e \tag{4}$$

It follows, therefore, that an exchange reaction leads to sharpening of the central part of the line. It must be borne in mind that at the ends of the line, where $|\Delta\omega| > \omega_e$, the signal retains the Gaussian form. A simple graphical method has recently been proposed for the determination of ω_e by the construction of linear transforms of Eqs. (2) and (3) [10]. The presence of exchange sharpening of the line provides a chemist with a reliable indication of the existence of fairly rapid (with a frequency of ω_e) displacements of an unpaired electron in the system. This effect is shown during the so-called transfer of the reaction center along a chain of conjugated bonds. The comparatively small width of the EPR signal of the Lorenz form from different carbons, in spite of the extremely high concentrations of unpaired electrons, indicates unequivocally the presence of a large number of highly conjugated systems. It is known that this conclusion is in complete accord with chemical and x-ray structural investigations of coals [11]. Analysis of experiments shows that the frequency of the exchange of electrons between neighboring condensed systems in coals is equal in order of value to $10^7 \cdot 1/\text{sec}$. The EPR lines of unpaired electrons in γ-irradiated albumens, where, as a result of delocalization of the electrons in the regular network of interchain hydrogen bonds, the EPR lines are narrowed ten-fold in comparison with the EPR lines of unpaired electrons in γ-irradiated individual amino acids [12], are another example of the occurrence of exchange.

The investigation of the so-called hyperfine nuclear structure of EPR spectra, caused by the reaction of the magnetic moment of an unpaired electron with the magnetic moments of nuclei containing in these particles, is of particular importance for the identification of the structure of complex radicals and paramagnetic complexes. As was shown by Gordy [13], nuclear hyperfine splitting in solids and solutions can be observed only as a result of an s-state admixture in the wave function of an unpaired electron. The number of components of hyperfine structure, the value of the splitting, the distribution of the intensity between the components, and the width of the individual components makes it possible, in a number of cases, to draw conclusions both with regard to details of the chemical structure and the distribution of the density of the unpaired electron between the different atoms inside the particle, the electronic structure of an atom with a given magnetic nucleus, and the reaction of a paramagnetic particle with the medium.

The spectrum of the methyl radical may serve as one of the simplest examples of the interpretation of EPR spectra with a hyperfine structure.

Fig. 1. EPR spectrum of the methyl radical (in irradiated polyaluminomethylsiloxane).

Figure 1 gives the spectrum of the radical (first derivative of the absorption line), obtained in our laboratory by irradiation of polyaluminomethylsiloxane

$$(-O-Si(CH_3)_2-O-\underset{|}{Al}-O-Si(CH_3)_2-O-Si(CH_3)_2-O-,$$

synthesized in K. A. Andrianov's laboratory (INÉOS, Academy of Sciences of the USSR)] with ultraviolet light at 77°K. Similar spectra were previously obtained by Matheson and Smaller [14] by irradiation of solid methane with γ-rays at 4.2°K.

As may be seen from Fig. 1, the spectrum consists of four individual components equidistant from each other and with an intensity ratio of 1: 3: 3: 1. The observed structure of the spectrum indicates that the moment μ_s of the unpaired electron (having a spin $s = {}^1/_2$) reacts with three identical nuclear moments μ_i, each of which has a spin $i = {}^1/_2$.

In actual fact, such a reaction leads to the appearance in the investigated system of four types of particles with somewhat different effective magnetic moments:

$\mu_s + 3\mu_i$ (a) $\quad \mu_s \quad \mu_i$ (c)

$\mu_s + \mu_i$ (b) $\quad \mu_s - 3\mu_i$ (d)

Since $\mu_i \ll \mu_s$ (approximately 10^3 times), the values of these effective moments are fairly similar, and the spectrum must consist of four components fairly close to each other.

From simple statistical considerations, it is clear that the probability of the existence of states (b) and (c) is exactly three times greater than that of states (a) and (d). From this, it follows that all the central components of the multiplet must have correspondingly greater intensities. For these reasons, in the investigated system, the spectrum shown in Fig. 1 may be due to the CH_3 radical only, because only in this particle is the free electron in the same position with respect to the three hydrogen atoms, each of which has a nuclear spin of ${}^1/_2$.

The detailed analysis of spectra with a hyperfine structure sometimes presents considerable difficulties, particularly in the case of a simultaneous reaction of an unpaired electron with dissimilar (H, D, N, F) nuclei, nonequivalent as regards position, and also in the case of superimposition of the spectra of several radicals or if the resolution is inadequate (if the widths of the individual component lines are equal to or greater than the distance between them). In such cases, however, when this analysis is possible, we obtain considerably more information on the structure of radicals than has been hitherto available in chemistry. Of particular importance is the fact that together with greater accuracy in our knowledge of the structure of the radical and the localization of the free valence in it – which, in principle could be achieved by other methods, e.g., chemical, although with great difficulty – EPR has made it possible to establish unequivocally a complete picture of the distribution of unpaired spin in a radical and, in a number of cases, solve the problem of the frequency of exchange of electrons between neighboring paramagnetic particles.

We will now examine some specific examples of work carried out in recent years in our laboratory of the use of EPR for the solution of chemical problems.*

2. Investigations of the Structure of Paramagnetic Particles

Negative aromatic ion-radicals, formed as a result of the transfer of an electron of an alkali metal in certain ester media to an aromatic molecule, are one of the most interesting investigations. A considerable amount of work on new reactions with participation of these particles has recently been published [15] and the accurate determination of their structure is, therefore, obviously of considerable interest to present-day chemical knowledge.

*Recent results obtained during investigations in the field of heterogeneous catalysis with this method will not be examined in this paper because they are to be published in this journal, in the form of original articles.

Fig. 2. EPR spectrum of the negative ion-radical of toluene.

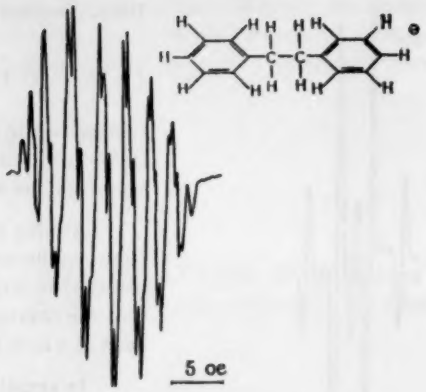

Fig. 3. EPR spectrum of the negative ion-radical of dibenzyl.

S. P. Solodovnikov and V. M. Chibrikin [16] have investigated the EPR spectra of negative ion-radicals of benzene and its derivatives obtained by dissolution of the corresponding molecules of dimethoxy ethane in the presence of potassium metal. The spectra of certain compounds of this type are also given by Tuttle and Weissman in [17].

The spectrum of the negative benzene ion consists of seven equidistant components with a binomial distribution of intensities 1: 6: 15: 20: 15: 6: 1. This result indicates that the unpaired electron is distributed uniformly over the whole benzene ring and reacts in the same way with all six hydrogen atoms. This result is fairly obvious but the data obtained with the toluene ion are not so readily interpreted. In this case, as with a number of other monoalkyl-substituted benzenes, the spectrum consists only of five components, with distribution of the intensities according to the law 1: 4: 16: 4: 1 (Fig. 2). From this, it follows that in negative ions with the general formula $(R-C_6H_5)^-$, the unpaired spin reacts with four equivalent hydrogen atoms. From an examination of the structural formulas, it follows that the unpaired spin is localized mainly in the ortho and meta positions of the phenyl ring and that the para position cannot be active in radical reactions.

Interesting results were obtained during the investigation of ions with the general formula $[Ph(CH_2)_nPh]^-$. As might be expected, in the diphenyl methane ion (n = 1) the free electron was distributed evenly between both aromatic rings, and as a result of the eight equivalent hydrogens in the ortho and meta positions gives a spectrum consisting of ten components. It is of far greater interest that this type of spectrum was also observed in the case of the 1,2-diphenyl ethane ion (n = 2) (Fig. 3). This is an unequivocal indication that even the $-CH_2-CH_2-$ group cannot completely exclude rapid transfer of the unpaired electron from one phenyl ring to another, because if the free spin were localized in one ring, the spectrum would obviously consist of five lines. From the values of the hyperfine splitting, expressed in frequencies, it follows that the lower limit for the frequency of exchange is 10^7 sec^{-1}. It is interesting that this value is close to the exchange frequency of unpaired spins between aromatic networks in carbons (see above), in which exchange evidently takes place in the aliphatic side chains connecting the individual networks with each other [11].

At n = 3 (in the ion of 1,3-diphenyl propane) the exchange frequency is so low that the hydrogens of both rings cannot be considered equivalent with respect to the unpaired spin, which is localized only in one ring; this leads to a spectrum consisting of five lines, similar to the spectrum of $(R-Ph)^-$ ions. This result does not, of course, exclude the possibility of the transfer of an electron between rings with frequencies of less than 10^7 sec^{-1}. Corroboration of this is obtained by taking measurements with longer waves.

The use of EPR is very effective for determining the structure of paramagnetic particles and radicals where it is impossible to say beforehand what conversions actually take place in the substance. This is particularly important when the process of radical formation takes place by the action of ionizing radiation, or exposure to

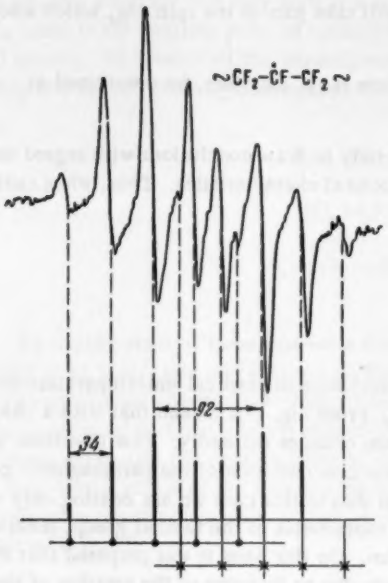

Fig. 4. EPR spectrum of a radical in irradiated teflon (under vacuum).

light, and in the solid phase. This fact virtually excludes completely the use of ordinary methods, for example, chemical, because for this purpose it would be necessary to convert the substance to liquid or gas, and during such a process, all radicals generally evaporate. The EPR method makes it possible to solve the problem of the structure of these radicals without disintegration of the investigated system.

We have already given spectra by way of example to prove that when polyaluminomethylsiloxanes are irradiated, the Si–C bonds are ruptured, with the formation of free methyl radicals.

When teflon (polytetrafluoroethylene) was irradiated by Co^{60} γ-rays, a fairly complex spectrum (Fig. 4) was found [18], which it was possible to interpret (see the lower part of this diagram) as the superimposition of two quintuplets with a binomial distribution of the intensities. On this basis, it may be assumed that the formula

$$\sim CF_2—CF_2—\dot{C}F—CF_2—CF_2\sim \qquad (I)$$

corresponds to this radical, stable up to 300° (under vacuum).

The occurrence of a doublet is due to the reaction with a fluorine atom in the α-position ($i_F = {}^1/_2$). The splitting of each component of the doublet into five components is due to the reaction of the spin with the four equivalent F atoms in the β-CF_2 groups.

The interpretation of the EPR spectra in irradiated polyethylene is interesting [19]. As a result of irradiation at low temperatures, a spectrum is observed, consisting of an even number of components (which indicates an odd number of hydrogen atoms, with which the unpaired electron reacts) with a splitting of about 25 oe, characteristic of alkyl radicals (see, for example, Fig. 1). When the polyethylene has been melted, or during irradiation at room temperature, a far narrower spectrum with a splitting of about 14-15 oe and, which is particularly important, an odd number of components is observed. On the basis of these data and complementary information, it was concluded that at low temperatures the C–H bond is ruptured and the alkyl radical

$$—CH_2—CH_2—\dot{C}H—CH_2—CH_2— \qquad (II)$$

is formed.

At the same time, as is well known [20], molecular cleavage (without the formation of radicals) of the molecular hydrogen takes place, with the formation of double bonds. At room temperature, migration of the free valence

$$\sim CH_2—\dot{C}H—CH_2—CH_2—CH_2\sim \longrightarrow \sim CH_2—CH_2—CH_2—\dot{C}H—CH_2\sim,$$

evidently takes place, leading to its localization in the energy-favorable allyl position:

$$\sim CH_2—\dot{C}H—CH{=}CH—CH_2\sim$$

In this radical, the structure of which is more accurately represented by the formula

$$\sim CH_2—\dot{C}H\cdots CH\cdots\dot{C}H—CH_2\sim, \qquad (III)$$

the unpaired spin is distributed evenly between two carbon atoms. This has the result that the splitting in its hyperfine structure is far less than in the case of radical (II). Moreover, since the density of the unpaired spin in the central atom is very low, an even number of hydrogen atoms will take part in the splitting, which also leads to an uneven number of lines of the hyperfine structure.

The structure of two types of radicals in irradiated polyethylene may, therefore, be considered as established.

Analysis of the EPR spectra sometimes makes it possible not only to draw conclusions with regard to the structural formula, but also to determine certain more detailed structural characteristics. Thus, when radical (I) reacts with oxygen, a peroxide radical

$$\sim CF_2-\underset{\displaystyle O-O}{\overset{|}{C}}F-CF_2\sim \qquad \text{(IV)}$$

is formed. Analysis of the relation between the form of the spectrum line of this radical and temperature made it possible to plan methods of determining the angle of C–O–O [21]. From Fig. 5 it is seen that with a change-over from room temperature to 77°K, the appearance of the spectrum changes markedly. This transition is completely reversible, since after repeated freezing and thawing the concentration of the paramagnetic particles does not change. This indicates that in this case we are dealing only with certain changes in the internal movements of the radical group, leading to the observed changes in the spectrum. On this basis it was proposed that these changes reflect the slowing down, due to freezing, of the rotation of the O–O group with respect to the direction of the C–O bond. A calculation made on the basis of this hypothesis gave a perfectly reasonable value of the C–O–O angle, i.e., 75± 15°. A value close to 75° is also obtained from an examination of the Briglebov atomic models for radicals of this type.

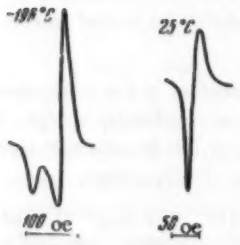

Fig. 5. EPR spectrum of the peroxide radical in irradiated teflon [a) at −196°; b) at 25°].

The disappearance of the anisotropy of rotation, observed during the freezing of samples of teflon with parallel chains (rolled films) [22], confirms the original hypothesis that the change in the spectrum of radical (IV) with temperature is due to freezing of internal movements.

3. Investigation of Conversions of Free Radicals

We will now examine the possibilities which the EPR methods opens up for the investigation of elementary reactions of free radicals. The existing limit of sensitivity ($\sim 1 \cdot 10^{13}$ liter/cm^3) does not make it possible as yet to investigate conversions of radicals during the course of ordinary rapid radical and radical-chain processes in a gaseous or liquid phase in which the maximum concentrations are generally not more than 10^{11}-10^{12} liter/cm^3. But, in certain cases, particularly during the reactions of radicals specially synthesized by some method or other in fair amounts, it has already been possible to obtain a number of new results.

N. I. Bubnov, S. F. Dyachkovskii, and A. E. Shilov [23] investigated the reaction of triphenyl chloromethane with lithium ethyl. During the course of this reaction, a marked increase in the concentration of the triphenyl-methyl radicals was recorded at first, subsequently falling until equilibrium was reached. This result indicates unequivocally that the free radical $(Ph)_3\dot{C}$ is formed during this reaction; this was the first direct confirmation of N. N. Semenov's hypothesis [24] that the formation of radicals during bimolecular reactions between molecules is possible. As a result of an analysis of the kinetic curves for the $(Ph)_3\dot{C}$ radical at different temperatures, it was possible to assess the activation energy of this new elementary process as 4-5 kcal/mole.

Measurement of the kinetic curves and equilibrium positions for the $(Ph)_3\dot{C}$ radical also made it possible to assess directly the activation energy of the recombination reaction of these radicals and its thermal effect [6]. The values obtained in this way were practically the same as those previously obtained by indirect chemical methods ($E \approx 7000$ cal/mole, $Q \approx 11{,}200$ cal/mole).

A detailed kinetic investigation of the reactions of radicals in the solid phase was carried out by way of the example of the above-described conversion of the fluoroalkyl radical (I) into the peroxide radical (IV) [25, 26]. In this case, the accuracy was very high as a result of the almost complete reversibility of the process up to temperatures close to the melting point of teflon (320°) and because both radicals give very good (completely distinguishable) spectra. As a result of this investigation, equations were obtained for the equilibrium constants of $R + O_2 \rightleftharpoons RO_2$ and for the velocity constants of the forward and reverse reactions. These equations are given below.

$$\dot{R} + O_2 \rightleftarrows R\dot{O}_2, \quad k = 10^{+23} e^{-\frac{14000}{RT}} \text{ cm}^3$$

$$R\dot{O}_2 \rightarrow \dot{R} + O_2, \quad k_1 = 10^{+8} e^{-\frac{20000}{RT}} \text{ sec}^{-1}$$

$$R + O_2 \rightarrow R\dot{O}_2, \quad k_2 = 10^{-15} e^{-\frac{6000}{RT}} \text{ cm}^3/\text{sec}$$

An examination of these equations shows that the energy of rupture of the bond in the peroxide teflon radical (C−OO) is 14 kcal/mole and that the equilibrium constant has roughly the same pre-exponential factor as for the majority of gaseous addition reactions. The fairly high activation energy of the addition process and the low values (compared with the gaseous phase) of the pre-exponential factors in the velocity constants are striking. Both these anomalies are evidently due to the fact that in the case of the addition reaction we are dealing, not with free displacement of the reacting molecules throughout the mass, but with markedly restricted diffusion of O_2 molecules towards immobile radicals and that, in consequence, instead of the ordinary velocity constant for bimolecular reactions

$$k \approx f\sigma^2 v e^{-E/RT} \approx f \cdot 10^{-10} e^{-E/RT} \text{ cm}^2/\text{sec}$$

(σ is the diameter of the molecule; $\underline{v}$ is the thermal velocity; f is the steric factor) we must use the equation $k = f \cdot D \cdot \lambda \cdot e^{-E/RT}$ cm³/sec, where D is the diffusion coefficient; λ is the mean free-path length, equal in our case to the mean interatomic distance (i.e., a value of about 10^{-8} cm). Direct measurements [25] have shown that for the diffusion of oxygen in teflon

$$D \simeq 2 \cdot 10^{-4} e^{-\frac{4600}{RT}} \text{ cm}^2/\text{sec}$$

Substituting this equation in the formula for $\underline{k}$, we obtain:

$$k_2 = f \cdot 2 \cdot 10^{-12} e^{-\frac{4600+E}{RT}} \text{ cm}^3/\text{sec}$$

By comparison with the experimental equation for k_2 given above, we find

$$f \simeq \frac{1}{2} \cdot 10^{-3}, \quad E_2 \simeq 1400 \text{ cal/mole}$$

which agrees completely with the ordinary values for radical reactions.

As regards the procedure for the solution of a number of new problems associated with the kinetics of radical conversions, it was very essential to design stable operating apparatus of high sensitivity [27], allowing measurements to be made while using ionizing radiation [28] or ultraviolet light [29]. To the best of our knowledge, such work has not been carried out abroad. Already after the first experiments it was found that an investigation during irradiation makes it possible to obtain far more complete information on the mechanism of primary processes than by the method of preliminary irradiation, previously employed [5]. This is due to the fact that during the course of irradiation, secondary processes leading to substantial blurring of the spectra often take place.

Complications resulting from secondary processes are also observed at low temperatures. Thus, for example, as a result of EPR measurements during the irradiation of the system $C_2H_5OH + H_2O_2$ with ultraviolet light at 77°K [30], it was possible to establish that the poorly reproducible EPR spectrum (observed by a number of authors [31, 32]) in this system, consisting of five poorly resolved components, is mainly the spectrum of the methyl radical, on which is superimposed a central line, appearing only after irradiation has been discontinued. By repeated switching on and off of the light it was possible to record completely reversible transition of the singlet to the quadruplet and vice versa, the dark reaction being the primary one. This made it possible to formulate the following mechanism of photolysis:

$$\left.\begin{array}{l} H_2O_2 + h\nu \longrightarrow 2\dot{O}H \\ \dot{O}H + CH_3CH_2OH \longrightarrow H_2O + CH_3\dot{C}H_2O \\ CH_3\dot{C}H_2O + h\nu \longrightarrow [\dot{C}H_3 + CH_2O] \end{array}\right\} \text{in the light}$$

$$[\dot{C}H_3 + CH_2O] \longrightarrow CH_3\dot{C}H_2O \qquad \text{in the dark}$$

The symbol $[\dot{C}H_3 + CH_2O]$ represents the $\dot{C}H_3$ radical and the CH_2O molecule present in one "cell" [33]. By the action of light, the equilibrium $CH_3CH_2O \rightleftharpoons CH_3 + CH_2O$ is displaced to the right and we observe a quadruplet of the $\dot{C}H_3$ radical. When the light is switched off, the reverse reaction takes place and a partial conversion of the quadruplet to the single line of the ethoxy radical is observed. It such a system is accepted, the CH_3 radicals must, in fact, disappear in the dark, according to the primary reaction.

SUMMARY

From this brief review of recent work on the use of the EPR method for the investigation of radicals it follows that this is now the most promising method for the investigation of free radicals in condensed media. In the few years since it was established, this method has made it possible to solve a large number of problems, which could not even have been raised when the old methods were employed. Its field of application is increasing continually and it can be stated with full justification that in the immediate future still greater successes will be achieved by the use of this method.

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CHAIN AND MOLECULAR REACTIONS OF INTERMEDIATES IN THE OXIDATION OF n-DECANE

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The rate constant for the breakdown of n-decyl hydroperoxides in n-decane containing α-naphthol has been compared with the rate constant for chain branching obtained by the inhibitor method to show that branching involves a nonchain decomposition of the peroxides into free radicals. The parallelism between the amounts of alcohol produced and hydroperoxides decomposed points to the formation of the RO radical as the elementary act in the breakdown of the latter compounds.

It has been shown that formation of free radicals (chain branching) proceeds along two parallel paths: monomolecular breakdown according to $ROOH \rightarrow RO + OH$, and bimolecular interaction between the hydroperoxide and the hydrocarbon according to $ROOH + RH \rightarrow RO + R + H_2O$. The rate constant for bimolecular chain branching increases with diminishing strength of the hydrocarbon R–H bond in the sequence: decane < isodecane < ethyl benzene < methyl oleate.

The alcohols and ketones produced in the oxidation of n-decane are consumed by chain reactions alone.

The study of the mechanism of hydrocarbon oxidation is one of the most important problems of chemical kinetics.

The complex chain reactions of oxidation give rise to numerous intermediate products which then undergo further transformations.

Thus, it is necessary to study the mechanisms of the reactions of these substances in the over-all oxidation with the special view of establishing whether the principal ones among them are chain or molecular processes.

Considerable quantities of hydroperoxides, alcohols, and ketones are found among the products of liquid-phase oxidation of n-decane [1].

The mode of reaction of these intermediates has been elucidated in the present work by adding α-naphthol, a strong inhibitor, to the reacting mixture to completely suppress the development of chain processes. This has made it possible to separate the chain reactions from the complex over-all process, so as to compare the consumption of the intermediate oxidation products by chain reactions and by molecular reactions.

Special attention was given to the reactions of the hydroperoxides, the chief branching agents in the n-decane oxidation [2], since a study of the breakdown of these compounds could furnish information on the mechanism of degenerative branching.

Most authors agree in considering the initial decomposition of the hydroperoxides to follow the reaction

$$ROOH \longrightarrow RO\cdot + \cdot OH \qquad (1)$$

N. N. Semenov [3], and a number of others, have pointed out that formation of free radicals by reaction between two saturated molecules may be more effective than mere monomolecular breakdown from the standpoint of the energy involved. Such will be the case if at least one of the bonds to be ruptured is not particularly strong and the bond which is formed has a high dissociation energy.

Since the R−H and RO−OH bond energies are lower than the H−O bond energy in water, it might be expected that free radicals could also be formed from hydroperoxide (degenerative branching) by bimolecular interaction of two saturated molecules, the reaction being either

$$2ROOH \longrightarrow RO_2\cdot + RO\cdot + H_2O \qquad (2)$$

or

$$ROOH + RH \longrightarrow R\cdot + RO\cdot + H_2O, \qquad (3)$$

The fact that the relation between rate of oxidation and hydroperoxide concentration is generally linear speaks in favor of Reaction (2). The reaction rate would be proportional to the square root of the hydroperoxide concentration if branching proceeded through monomolecular breakdown of the hydroperoxide according to Reaction (1).

The suggestion has been advanced [4] that the hydroperoxide breakdown at moderate concentrations is predominantly through the bimolecular reaction (2). The heat of reaction for bimolecular hydroperoxide breakdown is 9 kcal, this process being 26 kcal more exothermic than $ROOH \rightarrow RO\cdot + OH\cdot$, for which the heat of reaction is 35 kcal. Thus, it is most likely that degenerative branching results from interaction of the hydroperoxide and the hydrocarbon.

Since the heat of reaction depends on the strength of the C−H bond in the hydrocarbon molecule, there will be numerous cases in which Reaction (3) will be more highly favored than bimolecular interaction of two hydroperoxide molecules, especially since the oxidizing mixture is considerably more concentrated in hydrocarbon than in hydroperoxide.

Thus, the C−H bond strength in n-decane is 92 kcal so that the heat change accompanying Reaction (3) would be

$$Q = Q_{H-OH} - Q_{RO-OH} - Q_{R-H} = 116 - 35 - 92 = -11 \text{ kcal},$$

and this process would be 24 kcal more exothermic than Reaction (1). The heat of reaction would be positive for hydrocarbons in which the bond energy is less than 81 kcal.

Certain work has given indirect indication of the possibility of a bimolecular hydroperoxide, hydrocarbon reaction. We have shown [2] that chain branching in the n-decane oxidation follows a first-order law with respect to the hydroperoxide, in which the rate constant is represented by the equation $K = 6.8 \cdot 10^{-8} \exp(-24{,}800/RT)$. The value of the frequency factor is here considerably less than that which would be anticipated for monomolecular hydroperoxide breakdown.

A bimolecular mechanism for initial breakdown of a hydroperoxide has also been advanced in a recent paper devoted to the effect of the solvent on the rate constant for the elementary reaction of tetraline hydroperoxide decomposition [5].

The Mechanism of Breakdown of Intermediate Hydroperoxides

The oxidation of n-decane containing the inhibitor α-naphthol was studied with a view to demonstrating chain breakdown of the n-decyl hydroperoxides and establishing a quantitative relation between the molecular and chain decompositions.

Quantities of the inhibitor sufficient to completely suppress chain breakdown of the hydroperoxides were introduced at various stages of the reaction.

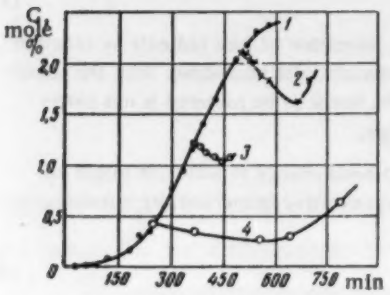

Fig. 1. Kinetic curves for the change in hydroperoxide concentration during oxidation of n-decane at 130°: 1) Without inhibitor; 2, 3, 4) with α-naphthol.

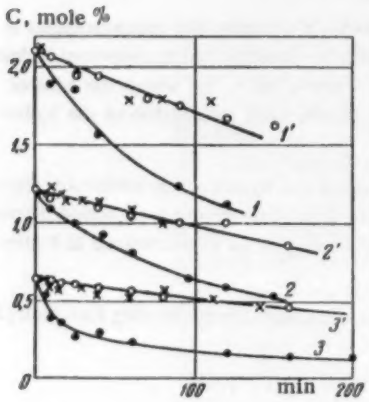

Fig. 2. Kinetic curves for the consumption of n-decyl hydroperoxides in n-decane in an atmosphere of nitrogen at 130°: 1, 2, 3) Without inhibitor; 1', 2', 3') with α-naphthol. The crosses on Curves 1', 2', and 3' designate hydroperoxide concentrations in experiments on the breakdown on n-decyl hydroperoxides in n-decane with added α-naphthol in an atmosphere of O_2.

The kinetic curves for hydroperoxide production show a sharp break after the α-naphthol is introduced and the chain reaction by which these compounds are formed is cut off. The hydroperoxide concentration does not remain constant after introducing the inhibitor, as it would if breakdown proceeded by chain reaction alone, but diminishes markedly. Thus, the hydroperoxides also decompose, at least in part, through a nonchain reaction which does not involve radicals. The rate constant for this nonchain hydroperoxide decomposition is independent of the initial concentration of these compounds and the presence of other oxidation products.

The same value of the rate constant, namely, $1.7 \cdot 10^{-3}$ min^{-1}, is obtained from Curves 2, 3, and 4 of Fig. 1, although each corresponds to a different time of introduction of the α-naphthol.

Thus, the rate constant for the nonchain hydroperoxide decomposition obtained by the method of inhibitors applies to the elementary breakdown of these compounds into radicals.

The hydroperoxide breakdown was studied, not only in the presence of an inhibitor, but also under conditions such that chain decomposition was unimpeded, the aim being to compare the rate constant for the elementary act of breakdown with the rate constant for the over-all reaction as measured in [6]. For this purpose the supply of oxygen was cut off at a definite hydroperoxide concentration and two parallel experiments on the kinetics of hydroperoxide consumption, the one with an inhibitor and the other without, then carried out in an atmosphere of nitrogen.

The kinetic curves of Fig. 2 show addition of inhibitor to lead to a marked retardation in the hydroperoxide breakdown so that free radical induced decomposition must occur under the conditions of oxidation of n-decane.

An important conclusion concerning the mechanism of inhibition can be drawn from this fact. Studies on the inhibition of oxidation usually assume that the naphthols react with the RO_2 radicals which propagate the chain. These radicals are not present, however, during the breakdown of the hydroperoxides in an atmosphere of nitrogen. Thus, α-naphthol reacts not only with the $RO_2 \cdot$ but also with other free radicals such as $RO \cdot$ which are formed in the hydroperoxide breakdown.

The ratio of the rates of the chain and the nonchain decompositions of n-decyl hydroperoxides in n-decane oxidation does not remain constant, but alters in parallel with the over-all rate of hydroperoxide decomposition as oxidation proceeds. The length of the chain in the hydroperoxide breakdown gives a quantitative characterization of this ratio which can be evaluated by comparing the rate constants for uninhibited breakdown and for breakdown in the presence of α-naphthol at fixed initial hydroperoxide concentration. When thus evaluated, the chain length for breakdown of n-decyl hydroperoxides in n-decane at 130° proves to vary from 20 steps at the beginning of reaction where the hydroperoxide concentration is 0.6% to three steps when this concentration has risen to 2.1%.

Figure 2 also includes results from experiments on the kinetics of nonchain breakdown of n-decyl hydroperoxides in n-decane in the presence of oxygen; these are in complete agreement with the data obtained in nitrogen and indicated that oxygen is without affect on the nonchain hydroperoxide breakdown.

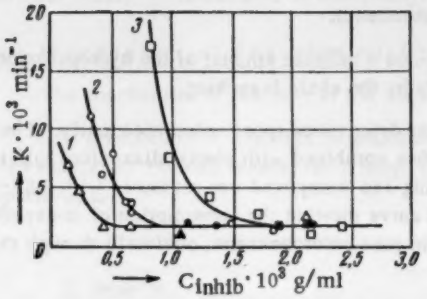

Fig. 3. Rate constants for the breakdown of n-decyl hydroperoxides in n-decane in an atmosphere of nitrogen at 130° plotted against inhibitor concentration:) Hydroperoxide concentration, 1) 0.63%; 2) 1.21%; 3) 2.1%. The shaded points correspond to similar experiments in an atmosphere of oxygen.

This last conclusion is confirmed by data on the rate constant for the breakdown of n-decyl hydroperoxides in n-decane containing the inhibitor at various concentrations (Fig. 3). This series of experiments shows that the rate constant for the hydroperoxide breakdown in nitrogen at first diminishes markedly as the α-naphthol concentration is increased but then becomes fixed once a certain inhibitor concentration is reached. This concentration is the higher, the higher the initial hydroperoxide concentration. The rate constant obtained with an excess of inhibitor applies to the nonchain hydroperoxide breakdown and is independent of the reaction conditions. Similar experiments in oxygen (shaded points in Fig. 3) lead to the same limiting value for the rate constant for the hydroperoxide breakdown.

The absolute value of the rate constant for the nonchain hydroperoxide breakdown varied between $1.7 \cdot 10^{-3}$ and $1.9 \cdot 10^{-3}$ min^{-1} in the different experiments. These values are close to the rate constant for chain branching in the n-decane oxidation ($K = 1.1 \cdot 10^{-3}$ min^{-1}) [2].

The fact that these constants do differ suggests that nonchain hydroperoxide breakdown into radicals is accompanied by molecular decomposition with the formation of ketones and water. This conclusion was tested in a special series of experiments on the breakdown in the presence of α-naphthol of n-decyl hydroperoxides which had been separated from the oxidized n-decane by the method of [7]. The products from this reaction were completely free of ketones. It is clear that the values of the constants which are under comparison differ by an amount which falls within the error of measurement of the two independent methods. This does not exclude the possibility that the somewhat lower value of the rate constant for chain branching might be due to the so-called "cell effect." A small proportion of the R· radicals formed through interaction of RO· and the solvent could react with the ·OH radicals without leaving the "cell."

The formation of RO·radicals in the nonchain hydroperoxide breakdown was confirmed by measuring the concentration of alcohols in the products from the breakdown of n-decyl hydroperoxides in nitrogen, using phenol at $8.5 \cdot 10^{-3}$ mole/liter as an inhibitor. The kinetic curves for hydroperoxide consumption and for alcohol formation are identical under these conditions. In other words, all of the alcohol obtained from the hydroperoxides is formed in subsequent reactions of the RO· radicals, a fact which is well illustrated by the following data:

Time from beginning of experiment, min	45	70	110	200	260
Hydroperoxides decomposed, mole %	0.1	0.24	0.40	0.61	0.96
Alcohols produced, mole %	0.1	0.26	0.38	0.64	0.94

These results indicate that chain branching in the n-decane oxidation involves a nonchain breakdown of the n-decyl hydroperoxides into radicals, one of which is RO· .

The Mechanism of Degenerative Branching

It has been pointed out earlier that branching can involve either monomolecular breakdown of the hydroperoxide molecules according to ROOH → RO + OH, or bimolecular interaction of hydroperoxide and hydrocarbon, ROOH + RH → R· + RO· + H_2O, with the formation of two radicals.

The rate of chain branching in the latter case should depend on the concentration of the hydrocarbon, n-decane.

Measurements were made on the rate of branching of n-decyl peroxides in chlorobenzene (chosen as an inert solvent) solutions and in mixed chlorobenzene, n-decane solutions. Decane containing the maximum concentration of hydroperoxides which can be obtained by oxidation was used in preparing the hydroperoxide, chlorobenzene solutions and the solutions in chlorobenzene and decane. This was first treated with K_2CO_3 to remove

acids and then reacted with a 10% aqueous NaOH solution at 0°. The resulting sodium salts were converted back into the free hydroperoxides by the action of concentrated H_2SO_4 and then extracted from the water layer by the solvent of desired composition (a mixture of n-decane and chlorobenzene).

The inhibitor was added to the system which already contained a definite amount of the hydroperoxides at a time when the radical concentration was determined principally by the chain branching.

The concentration of α-naphthol in the oxidized decane was determined spectrophotometrically. The α-naphthol in the sample was extracted twice with 1 N NaOH and then combined with phenyl diazonium sulfate. The intensity of the absorption maximum (520 mμ) of the resulting azo compound was measured with a SF-4 spectrophotometer. The rate of branching was obtained from the curve showing the consumption of α-naphthol. It was established that the hydroperoxide breakdown occurs even in pure chlorobenzene, obviously through the reaction ROOH → RO· + ·OH.

The rate of peroxide breakdown in chlorobenzene increases linearly with the n-decane concentration (Fig. 4, Curve 1), the indication being that the reaction is of first order in terms of the hydrocarbon. The same result would be anticipated if chain branching was assumed to be a bimolecular reaction.

Thus there are two parallel paths for chain branching in the oxidation of n-decane, one described by a monomolecular law and the other by a bimolecular law.

The rate constant for monomolecular breakdown, k_1, was determined from the experiments in pure chlorobenzene and has the value $1.68 \cdot 10^{-4}$ min^{-1}. The rate constant for the bimolecular hydroperoxide, n-decane reaction, k_2, was determined from the slope of Curve 1 (Fig. 4) and proves to be equal to $9.9 \cdot 10^{-6}$ mole$^{-1} \cdot$ min$^{-1} \cdot$ liter.

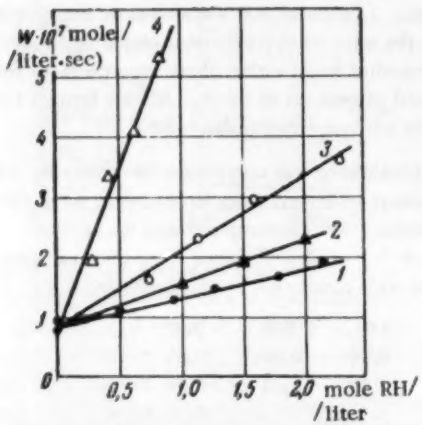

Fig. 4. The rate of branching plotted against hydrocarbon concentration in solutions of: 1) Chlorobenzene-decane; 2) chlorobenzene–isodecane; 3) chlorobenzene-ethyl benzene; 4) chlorobenzene-methyl oleate. Hydroperoxide concentration, 0.03 mole/liter. Temperature, 130°.

Thus, it was the effective rate constant for branching, a quantity which can be expressed in terms of the constants k_1 and k_2 through the equation:

$$k_{eff} = k_1 + k_2[RH],$$

which was measured in [2].

If [RH] in the oxidized n-decane is supposed to be 5.2 mole/ /liter and the rate constants are assumed to have the values obtained in the present work, the effective rate constant for branching will be

$$k_{eff} = 0.68 \cdot 10^{-3} \text{ min}^{-1}.$$

This result is in satisfactory agreement with the rate constant for branching obtained in [2], namely

$$k = 1.1 \cdot 10^{-3} \text{ min}^{-1}.$$

The relation between the rate of branching and the nature of the solvent was studied in experiments on the rate of hydroperoxide breakdown in solutions of chlorobenzene containing various amounts of isodecane, ethyl benzene, or methyl oleate.

The following rate constants for bimolecular branching were obtained from the slopes of Curves 1, 2, 3, and 4 in Fig. 4:

	$K \cdot 10^{+5}$ mole$^{-1} \cdot$ min$^{-1} \cdot$ liter
Chlorobenzene–decane	0.99
Chlorobenzene–isodecane	1.44
Chlorobenzene–ethyl benzene	2.46
Chlorobenzene–methyl oleate	9.96

It is clear that the rate constant for branching is the higher, the weaker the C–H bond in the hydrocarbon (n-decane, 92 kcal; isodecane, 88 kcal; ethyl benzene, 77 kcal) and the easier it is to oxidize the hydrocarbon.

The Mechanism of Reaction of Alcohols and Ketones

The mechanism of reaction of the alcohols and ketones was also studied.

The presence of α-naphthol caused certain difficulties in determining the alcohol concentrations in inhibited reactions. For this reason, the α-naphthol was replaced with phenol, another inhibitor, in this series of experiments.

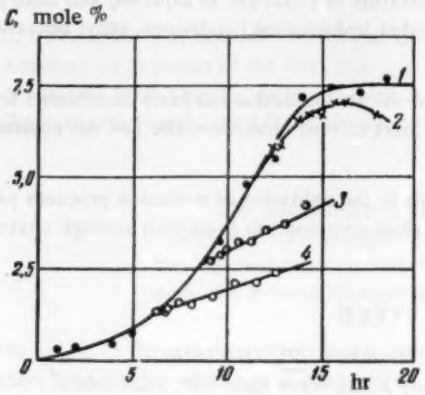

Fig. 5. Kinetic curves for the change in the alcohol concentration during oxidation of n-decane at 130°: 1) Without an inhibitor; 2, 3, 4) with phenol.

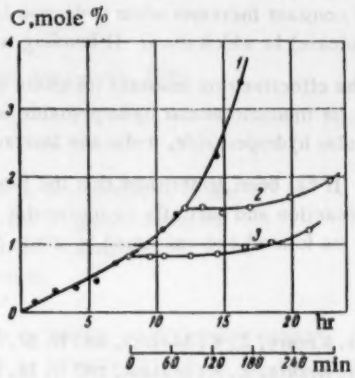

Fig. 6. Kinetic curves for the change in the ketone concentration during oxidation of n-decane at 130°: 1) Without an inhibitor; 2, 3) with α-naphthol.

Kinetic curves for the change in the alcohol concentration after introducing phenol at various stages in the oxidation of n-decane are presented in Fig. 5. Curve 1 of this same figure shows the kinetics of alcohol formation in the uninhibited reaction. The character of the kinetics alters markedly as soon as phenol is introduced, the alcohol content of the reacting mixture diminishing sharply. This indicates that the principal formation of alcohols in the oxidation of n-decane is through chain reaction, only an insignificant proportion arising from nonchain processes.

The consumption of alcohols also proceeds almost entirely through a chain process.

In fact, with an excess of inhibitor (Curves 3 and 4, Fig. 5) the alcohol concentration increases according to a linear equation and corresponds exactly with the amount of the hydroperoxides decomposing under these same conditions (see above). Thus, the alcohols remain unconsumed in a completely inhibited oxidation of n-decane.

A comparison with the kinetics of alcohol formation in the absence of a characteristic inhibitor for the intermediate reaction products justifies the conclusion that the consumption of alcohols in the n-decane oxidation is by chain reaction alone.

The ketone concentration remains constant until all of the added inhibiting α-naphthol has been consumed (Fig. 6). This indicates that the ketones are formed and consumed by chain reactions alone.

SUMMARY

1. Study has been made of the kinetics of breakdown of n-decyl hydroperoxides in n-decane containing α-naphthol. The rate constant for nonchain hydroperoxide breakdown has been compared with the rate constant for chain branching in the n-decane oxidation as measured by the method of inhibitors. The fact that these

constants have approximately the same value indicates that chain branching involves nonchain breakdown of the hydroperoxide molecules into radicals.

2. Comparison of the rate of nonchain hydroperoxide breakdown and the rate of formation of alcohols under identical conditions has led to the conclusion that the production of RO · radicals is the elementary act in the decomposition of the former compounds.

3. It has been established that α-naphthol, the oxidation inhibitor, interacts not only with the RO_2 · radicals, but with the RO · radicals produced in the hydroperoxide breakdown as well.

4. The hypothesis that free radicals are formed (chain branching) through bimolecular interaction of saturated hydroperoxide and hydrocarbon molecules has been confirmed. This conclusion follows from the relation between the rate constant for chain branching and the concentration of n-decane in solution, and from the fact that this constant increases when n-decane is replaced by another hydrocarbon (isodecane, ethyl benzene, or methyl oleate) in which the C–H bonding is weaker.

The effective rate constant for chain branching in the n-decane oxidation has been determined from the constant for monomolecular hydroperoxide breakdown in the inert solvent chlorobenzene and the constant for bimolecular hydroperoxide, n-decane interaction.

5. It has been established that the formation of alcohols in the oxidation of n-decane proceeds partially by a chain reaction and partially by molecular reactions, while their consumption is entirely through chain processes. Ketones are formed and consumed by chain processes alone.

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THE MECHANISM OF METALLIC OXIDE CATALYZED OXIDATIONS

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The tracer method has been used to show that metallic oxide oxidation catalysts make no contribution to the oxygen content of the reaction products and the actual mechanism of catalysis is, therefore, not a two-step oxidation-reduction process.

The oxides of the transition elements are typical catalysts for oxidation by molecular oxygen. As a rule, these oxides are readily reduced, and even more easily regenerated by gaseous oxygen, at the temperature of catalysis. It is generally assumed that these oxidation-reduction processes also occur when the catalyst is flushed out with the gaseous mixture of oxygen and reducing agent, alternating one with the other and thereby accelerating reaction in the mixture. A two-stage oxidation-reduction mechanism of oxidation catalysis based on these facts is accepted widely at present even though there are numerous indirect indications (which we will not stop on here) of its doubtful validity.

The tracer method has made it possible to check the validity of this mechanism directly. According to this mechanism, there should be a rapid equalization of the isotopic compositions of the gas and a catalyst whose oxygen has been replaced with the O^{18} isotope, each elementary cycle resulting in the substitution of an oxygen atom of the catalyst lattice by another oxygen atom from the gaseous phase.

The present article is a brief summary of work carried out in the author's laboratory, where tracer O^{18} has been used in testing this proposed mechanism for various catalysts and for various typical oxidation processes.

1. Catalytic Oxidation of CO on MnO_2 [1]

Active MnO_2 enriched in O^{18} was obtained by oxidizing heavy $Mn(OH)_2$ by chlorine. The residue was carefully washed with water containing heavy oxygen and then dried in vacuum while gradually raising the temperature to 550°. When so dried, the catalyst did not undergo oxygen exchange with either air or carbon dioxide at temperatures below 180°. The O^{18} content of the catalyst was determined from the density of the water resulting from its reduction with hydrogen.

TABLE 1

Exp. No.	Amount of product CO_2, g	O^{18} content of catalyst ($\gamma \cdot 10^{-6}$ g) after catalysis
1	1,492	99
2	1,442	104
3	3,220	97
4	1,973	96

The dried catalyst in a reaction tube was placed in a furnace where it was held at constant temperature and through it a mixture of dry air and carbon dioxide (~ 2%) was passed at such a rate as would assure ~ 25% oxidation. The initial O^{18} content of the catalyst was 99 γ, the charge of catalyst weighed 2 g, and the working temperature was 178°. Table 1 shows that the O^{18} content of the catalyst remained essentially unchanged even though the amount of oxygen reacting at the surface was commensurate with the entire oxygen content of the oxide charge. There was no indication

of the exchange which would be anticipated if reaction proceeded through a mechanism of alternate oxidation-reduction in the catalyst. In Experiment 4, a part of the air was replaced by nitrogen while holding the partial pressure of CO constant. There was no exchange even in this case, although a certain reduction of the catalyst was observed. It is clear that oxidation and reduction of the catalyst proceed much more slowly than catalysis itself, if they occur at all, and they cannot, therefore, be steps in the catalysis.

2. Catalytic Oxidation of CO on CuO [2]

The experimental procedure here was similar to that described above. The CuO was prepared from $Cu(OH)_2$ which had been precipitated from a solution of $CuCl_2$ and NaOH in water containing heavy oxygen. Dehydration was carried out in vacuum while the temperature was raised to 500°. The resulting CuO^{18} did not undergo oxygen exchange with air or CO_2 at temperatures below 300°. The microflotation method was used to determine the density of the water obtained by reducing the catalyst with hydrogen. The initial O^{18} content of the CuO was 109 γ, the amount of oxygen in the CuO charge was 0.2 g, and the working temperature was 300°. Results are presented in Table 2. It is clear that exchange did not occur even in those experiments in which the amount of reacted oxygen was seven times greater than the oxygen content of the catalyst charge. Obviously, a mechanism of alternate oxidation and reduction of the catalyst is not valid even here.

TABLE 2

Exp. No.	Duration of expt., hr	Amt. of bound oxygen, g	O^{18} content of CuO after catalysis, γ
1	16	0,8	110
2	22	1,0	114
3	28	1,4	109

TABLE 3

Catalyst No.	Time of passage of air, hours	O^{18} content, γ	
		in I fraction of water	in II fraction of water
1	22	57	65
1	22	59	66
2	18	65	73
2	18	65	69

The validity of these conclusions can be questioned on the ground that catalysis proceeds only on active centers which make up an infinitesimally small proportion of the mass of the catalyst and thus escape observation. This objection was proven unfounded by a special series of experiments designed to show the high mobility of oxygen in the oxide lattice.

These experiments were based on a differential isotopic method similar to that of Keier and Roginskii [3]. The catalyst was reduced to highly dispersed metallic copper by hydrogen, half oxidized by heavy oxygen at 300°, and oxidation then completed in ordinary oxygen. Following this the sample was held in a current of air at this same temperature for the same length of time as was commonly allowed for the catalyzed reactions. The catalyst was then reduced with hydrogen and separate isotopic analyses carried out on fractions I and II of the product water (Table 3). The table shows the isotopic composition of these two fractions to be practically identical, which is to say that the O^{18} becomes uniformly distributed throughout the entire crystalline mass during the course of the catalytic experiments. Such migration of oxygen throughout the crystal would assure that exchange would embrace a sufficient volume of the crystal to be detectable to analysis in our experiments, even if this exchange were to be limited to a small proportion of the catalyst surface.

3. Catalytic Oxidation of Naphthalene on V_2O_5 [4]

Heavy vanadium pentoxide was prepared by exchange between V_2O_5 and water vapor enriched in O^{18} at 550°. This catalyst did not undergo exchange of oxygen with the air at temperatures below 450°. A mixture of air and naphthalene vapors at a concentration of $25.6 \cdot 10^{-5}$ mole/liter was passed over the catalyst at 320-390°C at 0.1 liter/min. The catalyst was unloaded at the end of the run and reduced by hydrogen to V_2O_3. The isotopic composition of the resulting water was determined by mass spectrometry. The results are presented in Table 4, from which it is seen that exchange could not be detected in this system.

Here, there is little likelihood of localized exchange at active centers, since the work of Farkas [6], and Boreskov and collaborators [5], has brought out that oxygen migrates through the V_2O_5 lattice with relative ease.

TABLE 4

Temperature, °C	Duration of catalysis, hours	Amount of oxygen in catalyst charge, g	Amount of oxygen bound in the course of catalysis, mole	Increment of density in water obtained by reducing catalyst, γ	
				original catalyst	after catalysis
320	30	0,0125	0,0256	700	710
340	30			710	690
380	42	0,0275	0,0320	530	550
	42			530	570
	42			470	510
380	34	0,0210	0,0510	730	720
390	34			715	715

TABLE 5

Isotopic Composition of CO_2 Obtained by Decomposing Oxygen-Containing Compounds on V_2O_5 (γ)

Exp. No.	I fraction	II fraction
1	250	240
2	200	190
3	200	180

The following experiments were set up to give further confirmation of the adequacy of the oxygen mobility in this oxide. The heavy vanadium pentoxide was treated with naphthalene vapors at 390°. This led to the formation of oxygen-containing compounds on the V_2O_5 surface, the oxygen coming from the V_2O_5 itself. These compounds were decomposed and the product CO_2 frozen out and subjected to mass-spectrometric analysis. The part of the catalyst which had been reduced in this operation was reoxidized at the same temperature by light oxygen and the catalyst subjected to the same operations as before to obtain a second fraction, II, of CO_2. Comparison shows the isotopic content of fractions I and II of the CO_2 (Table 5) to differ only insignificantly so that the light oxygen deposited on the surface prior to the second operation must have succeeded in distributing itself throughout the entire volume of the crystal. It is clear that this same extension of exchange into the body of the crystal would occur even if exchange in catalysis were limited to a small portion of the surface. Thus inability to detect exchange during catalysis is definite evidence against an oxidation-reduction mechanism of catalysis in this system also.

5. Catalytic Oxidation of SO_2 on V_2O_5 [7]

The oxidation of SO_2 and SO_3 on V_2O_5 proceeds with appreciable velocity only at temperatures in excess of 500°. Direct exchange of the oxygen of the V_2O_5 and the oxygen of the gaseous phase is observed at this temperature. Two series of experiments were carried out in order to obtain an answer to the question which has been posed in this work. The first series involved a comparison of the rates of oxygen exchange of the catalyst charge with air free of SO_2, and with a mixture of air and SO_2, i.e., in the course of the catalytic surface reaction. On the basis of the mechanism of alternate oxidation-reduction in the catalyst it could be anticipated that catalysis would markedly increase the rate of exchange. The second series of experiments involved a quantitative study of the kinetics of exchange between V_2O_5 and gaseous oxygen, with a comparison of the rates of exchange and catalysis under identical conditions.

TABLE 6

Material analyzed	Temperature of exchange, °C	Increment in density of water from reduction, γ	Exchange, %
Original V_2O_5		375	
After exchange with air	580	290	22
After catalysis	580	300	20

The V_2O_5 for the experiments of the first series was obtained by oxidizing V_2O_5 with heavy oxygen at 500°. The O^{18} content of the V_2O_5 was determined from isotopic analysis of the water resulting from its reduction with hydrogen, using either the mass-spectrometric or the microflotation method. The results are presented in Table 6.

These data make it clear that the degree of exchange in catalysis at 580° is essentially the same as that observed with pure air, even though catalysis proceeds quite intensively at this temperature. Obviously, catalysis is not accompanied by that increase in the rate of exchange which would be anticipated on the basis of a mechanism of alternate oxidation and reduction in the catalyst. The improbability of such a mechanism is further indicated by the comparison of the kinetics of exchange in V_2O_5 with the rate of catalysis on the same samples (second series of experiments).

Tablets of analytical grade pentoxide were dried to constant weight at 200°. The charge of V_2O_5 was then loaded into an exchange system equipped with a circulatory pump and there aged, first in vacuum at 300°, and then in dry air at 450°. Following this, the air was pumped out and replaced with dry heavy oxygen, the furnace was heated, and the exchange studied. Analysis of the specimens of gas was by mass spectrometry. Results on the kinetics of exchange are presented in Table 7.

It is known that V_2O_5 can readily lose a small proportion (< 1%) of its oxygen without forming a new phase. It is thus natural to suppose that exchange occurs through the dynamic equilibrium:

$$V_2O_5 \rightleftarrows V_2O_{5-n} + \frac{n}{2} O_2.$$

Designating the rates of forward and reverse reactions in the equilibrium state by W, the mole fraction of O^{18} in the gaseous phase by $\underline{y}$, and in the oxide, by $\underline{x}$, and the total amount of oxygen in the gaseous phase by V, and in the catalyst charge, by $\underline{v}$, one can readily obtain the following equation for the rate of exchange:

$$\frac{dy}{dt} = \frac{W}{V}[y_0 - y(1+\lambda)].$$

where $\lambda = \frac{v}{V}$. This can be integrated from y_0 to $\underline{y}$ and from 0 to $\underline{t}$, to give:

$$\lg \frac{\lambda y_0}{(1+\lambda)y - y_0} = \frac{W(\lambda+1)}{2{,}3v} t = kt$$

The data are in good agreement with the predictions of this equation. The rate of dissociation of V_2O_5, W, was calculated from the values of $\underline{y}$. Specific values referred to 1 g of V_2O_5, W_{spec}, for various temperatures are given in Table 8: the energy of activation calculated from them proves to be 37 kcal/mole.

TABLE 7

Exchange Kinetics

Experimental conditions	t, hrs	y^* (τ)	t, hrs	y (τ)	t, hrs	y (τ)
	0	1125	0	1116	0	1172
	1	878	1	981	1	1125
	3	702	2	963	3	1098
	6	554	4	810	6	1062
	8	558	6	711	9,5	972
			8	680		
	∞ (calc)	410	∞ (calc)	408	∞ (calc)	447
T°C	580		550		500	
Charge of V_2O_5, g	1,93		1,85		1,89	
$P_{initial}$, mm	388		363		394	
P_{final}, mm	365		358		358	

*Here $\underline{y}$, the O^{18} content of the gaseous phase, has been expressed in terms of the increment of density of the water.

TABLE 8

T,° C	$W_{spec.}$, ml/(hr · g)
500	3,03
550	12,8
580	27,3

The rate of catalysis of a 4.4% mixture of SO_2 and air was measured on these same samples of V_2O_5. The rate at 500° corresponds to the consumption of 30 ml O_2/(hr · g), while the value of W_{spec}, the rate of the process responsible for exchange, is only one-tenth as large, or 3 ml O_2/(hr · g) (Table 8).

If catalysis followed an intermediate oxidation-reduction mechanism such as:

$$1)\quad SO_2 + \frac{1}{n} V_2O_5 \rightleftarrows SO_3 + \frac{1}{n} V_2O_{5-n}$$

$$2)\quad \frac{1}{n}\left(V_2O_{5-n} + \frac{n}{2} O_2 \rightleftarrows V_2O_5\right),$$

the second step in which the catalyst is regenerated would be identical with the reverse of the oxygen exchange reaction. It is true that the first step here does not correspond to the first step in the exchange reaction, oxygen being removed from the V_2O_5 by molecular SO_2 in catalysis and evolved in the free state by dissociation in exchange. There is considerable reason for assuming, however, that reduction of V_2O_5 by sulfur dioxide proceeds more slowly than dissociation. Our value for the activation energy of dissociation (37 kcal/mole) is actually almost identical with the activation energy for the catalytic oxidation of SO_2 on V_2O_5 (36 kcal/mole) [8], so that the frequency factor must be less for dissociation than for reduction. If correct, this last conclusion would indicate that the rate of a hypothetical sulfur dioxide catalysis through a mechanism of alternating oxidation-reduction of the V_2O_5 should be much lower than the rate of oxygen exchange which, in turn, is only one-tenth as large as the measured rate of catalysis. Thus a comparison of the rates of exchange and sulfur dioxide catalysis also speaks against a mechanism of alternate oxidation and reduction in the catalyst as the principal path for the catalyzed reaction.

SUMMARY

None of the metallic oxide catalyzed processes which we have studied involves oxygen exchange between the oxide and the gaseous phase such as would be anticipated for a mechanism of alternating oxidation and reduction in the catalyst. Clearly, this does not represent the true reaction mechanism.

In addition, simultaneous presence of two reaction components will prevent extensive interaction of either with the catalyst. The oxygen exchange involved in these processes would have been detected in our experiments if each component reacts with the catalyst during the catalyzed reaction just as if it were present alone. The chemical changes in the catalyst which do occur in the course of the catalyzed chemical process, e.g., partial reduction of V_2O_5 in the oxidation of naphthalene and partial reduction of CuO or MnO_2 in the oxidation of CO with a moderate excess of oxygen, do not lead to an appreciable oxygen exchange, either because they proceed too slowly or operate in the one direction only. These processes fix the stationary state of the catalyst and play a vital role in catalysis, but they are not essential factors in determining the reaction mechanism.

We are inclined to think that similar relations between the interaction of each reactant with the catalyst, in the absence of its reaction partner and during the catalyzed reaction, must apply to other catalytic processes as well. In a given stage of the catalytic process, the two components of the elementary act combine with the catalyst with minimal activation energy to form a complex which subsequently breaks down to give the reaction products and free the catalyst once more. Thus, the formation of active binary complexes between the individual reaction components and the catalyst with eventual production of a chemical compound can be expected at the catalytically active centers only if the formation of still more involved complexes is strongly inhibited for some reason (by the absence of one of the reaction partners, for example), or if the system is in that temperature range where the free energy of formation of a bulk or surface compound involving some one reactant and the catalyst is more negative than the free energy of reaction between the components themselves. These sectors of the catalyst fall out of the normal catalytic cycle in the latter case.

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THE MECHANISM OF ISOTOPIC EXCHANGE OF HYDROGEN ON PLATINUM FILMS

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We have investigated the isotopic exchange in molecular hydrogen, and also the exchange of adsorbed hydrogen with gaseous hydrogen on platinum films at 78°K and 90°K, using deuterium and tritium.

Evidence has been found of inhomogeneity of the platinum surface with respect to hydrogen adsorption. The partition coefficients of the hydrogen isotopes on adsorption have been determined. On the basis of measurements of the kinetic isotopic effects, the exchange reaction has been shown to be molecular in character, and possible mechanisms for the process are discussed.

A large number of investigations have been devoted to the study of the isotopic exchange in molecular hydrogen on solid catalysts, and in the majority of these, the probability of two mechanisms has been the topic of discussion. These mechanisms are adsorption-desorption (Bonhoffer-Farkash), and a chain process (Eley-Raidil).

According to the former of these mechanisms, the exchange reaction, $H_2 + D_2 \rightleftharpoons 2HD$, is accomplished by means of the adsorption of molecules of hydrogen, accompanied with dissociation into atoms, and subsequent redistribution of the atoms on desorption. According to the chain mechanism, the exchange occurs as a result of the interaction of molecules of hydrogen with atoms which are adsorbed on the surface of the catalyst. The matter is complicated by the fact that, even on the same catalyst, the exchange reaction may vary with the conditions and proceed by different mechanisms. Thus, on platinum catalysts, the activation energy of the exchange reaction at temperatures above 350°K attains a value of 7.5 kcal/mole, while at low temperatures (78°-270°K) it amounts to only 0.5 kcal/mole. In this case, too, the pre-exponential factor at low temperature is less by five orders of magnitude than at high temperatures [1].

We have in the current work undertaken the task of attempting to elucidate the mechanism of exchange in the low temperature region. With this in view, we have studied the exchange rate between hydrogen adsorbed on platinum, and molecular hydrogen. Eley [2] has already used this method with success using deuterium, and the method has also been employed by A. Farkash and L. Farkash[3], and especially by G. Schuit [4].

We have been able to increase the precision of measurement of the rate of exchange by using tritium, and also to estimate the valuesof the thermodynamic and kinetic isotopic effects.

Method of Investigation

1. Description of the plant. The plan of the apparatus which we have used is depicted in Fig. 1. Hydrogen and deuterium were obtained by the electrolytic decomposition of water and of 99.7% deuterium oxide, respectively. In both cases, the gases were purified from oxygen on a palladium catalyst, and dried over silica gel, and final purification from water vapor, nitrogen and other impurities present in the electrolyte was carried out in carbon traps chilled by means of liquid nitrogen. In the experiments using deuterium, the analysis of the gas was carried

out by a thermal conductivity method [5], using the tubes 11, which contained a platinum filament of diameter 20 μ and length 100 cm. Traps chilled by means of liquid nitrogen were used to protect the tubes from any contamination by the vapors of oil or mercury, which would vitiate the results at low pressures. The delivery tubes at the level of the liquid nitrogen were protected by means of evacuated and silvered jackets, and because of these any change in the level of the liquid nitrogen Dewar vessels had no effect on the gas pressure in the system.

Tritium was stored in the form of uranium hydride in a metallic container. The 60% tritium which was evolved on heating was not submitted to further purification, since uranium combines irreversibly with nitrogen, oxygen and other possible impurities [6]. The content of tritium in the hydrogen was determined by means of the external attached chamber 4 [7]. The expended tritium was drawn off by means of the Langmuir pump 5 into the carbon trap 6, which was chilled in liquid nitrogen; from this it was periodically transferred into the container 7, where it was absorbed by means of uranium.

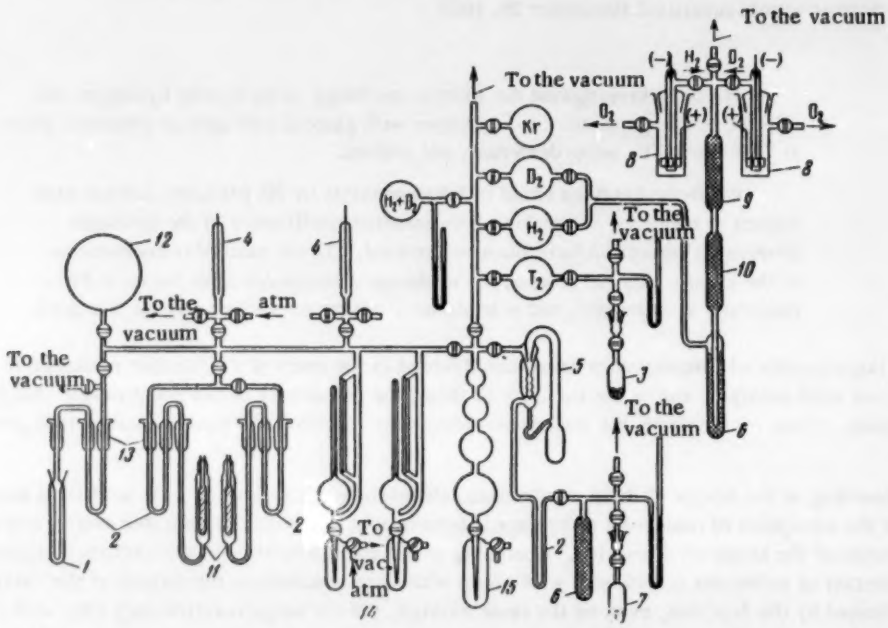


Fig. 1. Plan of the apparatus. 1) Reaction vessel; 2) traps; 3) container for UT_3; 4) chambers for tritium analysis; 5) Langmuir pump; 6) carbon traps; 7) vessel for storing expended tritium in uranium; 8) electrolysis apparatuses; 9) palladium catalyst; 10) silica gel; 11) tubes for deuterium analysis; 12) reserve volume; 13) silvered jackets; 14) MacLeod manometers; 15) burette.

Spectroscopically pure krypton was used for the determination of the surface area of the films by adsorption at the temperature of liquid nitrogen [8].

The MacLeod manometer 14 was used to determine pressure between 10^{-4} and 3 mm Hg. The burette 15 was employed for adsorption measurements, and in certain cases was also used as a Tepler pump.

Before experiments were carried out, the entire apparatus was evacuated at a pressure of 10^{-7} mm Hg.

2. Preparation of the platinum films. The platinum films were prepared in a glass vessel of diameter 25 mm and height 110 mm provided with molybdenum leads, to which was welded a wire of diameter 0.3 mm and length 220 mm, made of "extra" grade platinum. Before film deposition the reaction vessel was evacuated for a long period while being heated to 400°, and the platinum wire was heated to a temperature close to the atomizing

temperature for platinum. The film deposition was carried out by heating the platinum wire by means of a carefully stabilized current of around 4 amp, under a potential of about 8 v, with continuous evacuation. The residual pressure in the vessel under these conditions amounted to only 5×10^{-8} mm.

During the deposition, the walls of the vessel were cooled with water at a temperature of 20°. Deposition under the conditions stipulated for a period of 8 hr permitted the production of films of weight 50 mg, having a total surface of around 3000 cm^2 for an apparent surface of 85 cm^2. The mean diameter of the crystallites was 470 A.

In order to avoid changes in the properties of the films during the subsequent studies of the hydrogen exchange, they were heated at 150° for a period of three hours. The effect of the heating was to reduce the area of the films by a factor of 2.5, and to increase the diameter of the platinum crystallites to 1170 A. The coefficient of roughness of the films was on the average 14.

Adsorption of Hydrogen

Figure 2 gives the adsorption isotherms for molecules of hydrogen, deuterium, and tritium at 90°K on different platinum films prepared under identical conditions. The inclination of the tritium isotherm to the axis of ordinates was attributed to the presence of a small impurity of He^3 formed through the radioactive decay of the tritium. When this circumstance is taken into account, there is no difference between the adsorptions of the hydrogen isotopes. At low pressures, the isotherms practically coincide with the axis of ordinates. After the adsorption of approximately 6×10^{14} molecules per 1 cm^2 of the film the isotherms curve abruptly, and further increase in pressure gives a curve with only a slight inclination to the axis of abscissas. Comparison of the adsorption isotherms of the hydrogen isotopes obtained at 78° and 90°K has revealed good agreement between them.

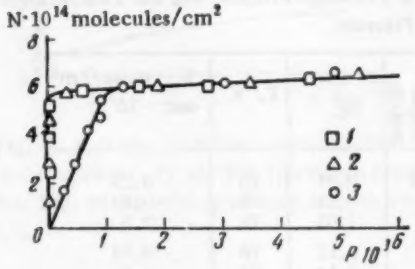


Fig. 2. Adsorption isotherms for the isotopes of hydrogen at 90°K. 1) H_2; 2) D_2; 3) T_2 + + He^3.

The surface of the films was subjected to a preliminary measurement with respect to its adsorption of krypton at the temperature of liquid nitrogen. The area occupied by a single atom of krypton was taken as 18.5 A^2. For all three isotopes, the horizontal part of the isotherm corresponded to the adsorption of 5.9×10^{14} molecules of hydrogen per 1 cm^2, which corresponds to an area of 16.9 A^2 per single molecule of adsorbed hydrogen, in good agreement with the data of N. N. Kavtaradze [9].

After evacuation of the film to a pressure of 10^{-7} mm Hg at 150°, the adsorption isotherm of hydrogen is completely reproducible, pointing to the complete removal of the adsorbed hydrogen from the platinum surface under these conditions, as had been shown earlier by N. N. Kavtaradze [9]. The use of tritium made it possible for us to determine with sufficient accuracy the quantity of hydrogen removed from the film during the desorption process. It appeared that on heating to 150°, only about 70% of the hydrogen was transferred to the gas phase from the surface. The remaining quantity of hydrogen must therefore under these conditions pass into the interior of the metal.

Isotopic Exchange in Molecular Hydrogen.

1. The sequence in which the experiments were carried out. The isotopic exchange in molecular hydrogen has been studied at 78° and 90°K, in the pressure range from 10^{-2} to 1 mm Hg.

In order to eliminate errors due to changes in the composition of the reacting mixture as a result of different adsorption of protium and deuterium on the platinum, there was first of all introduced into the reaction system a stoichiometric mixture of H_2 and D_2, and this was then maintained at the temperature of the experiment until adsorption and exchange were quite complete. The reaction vessel was then isolated from the rest of the system, and then the equilibrium mixture was completely removed from the latter, and replaced by a new mixture of H_2 and D_2. The same mixture was also fed into both gas analysis tubes.

The pressure of the gaseous mixture in the bulk, and in the tubes, was exactly the same as that in the reaction vessel. In this position, the needle of the galvanometer in a bridge circuit, to which the gas analysis tubes were connected, was set at the zero position. Before the commencement of exchange, one of the tubes was disconnected by means of its tap from the remaining volume, and was used as a standard. Exchange began from the moment when the reaction vessel was connected to the volume of the gases, and the calculation of time commenced from this moment, together with the change in the position of the galvanometer needle. The lamps had been calibrated beforehand, the number of galvanometer divisions corresponding to equilibrium transformation being thus known. The bridge circuit permitted the measurement of the degree of transformation to an accuracy of 5%.

The specific rate constant of the isotopic exchange reaction was calculated from the equation [1]:

$$k_{sp} = \frac{N}{S_t} \frac{2{,}3}{t} \lg \frac{n_\infty - n_0}{n_\infty - n_t} \text{ mole/cm}^2\cdot\text{sec}$$

where N is the number of moles of gas in the system; S is the surface area of the film, in cm^2; t is the time during which contact occurs, in sec; n_∞ is the number of galvanometer divisions corresponding to complete transformation; n_0 is the number of galvanometer divisions at the initial moment; and n_t is the number of galvanometer divisions at time t.

2. Results obtained. Figure 3 gives the rate of isotopic exchange in molecular hydrogen ($H_2 + D_2$) at 78° and 90°K, and at a pressure of 0.12 mm Hg. The time of half-change from equilibrium amounts to 7 min at 90°K and 17 min at 78°K.

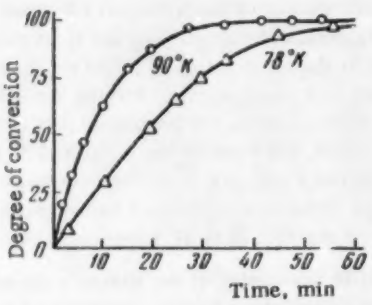


Fig. 3. Rate of isotopic exchange between molecules of H_2 and D_2 at 78°K and 90°K, and at pressure of 0.12 mm Hg.

TABLE 1

Relationship Between the Specific Rate Constant of the Exchange Process, and the Temperature and Pressure

Series of experiments	P, mm Hg	T, °K	k_{sp}, mole/cm³·sec · 10^{-11}
I	0,01	78	0,29
	0,12	78	0,92
	1,03	78	2,5
II	0,12	78	0,78
	0,12	90	2,3

Table 1 gives the values of the specific rate constants for the exchange process, obtained under various conditions. The investigations were carried out on the same film. Series I of the experiments was carried out before, and series II after, the study of exchange with adsorbed hydrogen.

The value of the specific rate constant obtained at a pressure of 0.12 mm and a temperature of 78°K is satisfactorily reproduced in the second series of experiments. The activation energy amounts to 1200 cal/mole. The order of the reaction in relation to the hydrogen pressure is 0.5.

Exchange Between Adsorbed Tritium and Molecular Hydrogen

1. The sequence in which the experiments were carried out. The rate of isotopic exchange between tritium adsorbed on a platinum film, and molecular hydrogen, has been studied at 78°, 90°, and 162°K, at hydrogen pressures of 0.1 and 1 mm Hg. The experiments were carried out on different film samples, though several experiments were carried out on one specimen, the adsorbed tritium being changed. After the preparation of the films for the experiment (by evacuation at a pressure of 5×10^{-3} mm Hg and heating to 150°C for two hours),

the film was cooled to the temperature of the experiment, and adsorption of tritium was carried out. Hydrogen containing 60% tritium was allowed to stand over the film for several days, with the object of attaining equilibrium with respect to the tritium between the adsorbed and molecular hydrogen. The hydrogen was then evacuated from the reaction space for three minutes at a pressure of 10^{-7} mm Hg. At temperatures of 78° and 90°K we did not observe any appreciable removal of hydrogen from the film. According to the data of N. N. Kavtaradze [9], at a temperature of 78°K the reversible adsorption of hydrogen amounts to 5% of the total adsorption.

After the evacuation of the reaction space, pure protium was introduced into it, and removal of samples of gas into the chamber was carried out periodically, so as to determine the concentration of tritium in the gas phase.

Before the removal of a sample, the chamber was evacuated to a pressure of 10^{-7} mm Hg. The sample was removed from the reaction space, where the pressure was about 0.1 mm Hg, and the chamber was supplied with dry air and the ionization current measured.

2. Results obtained. Figure 4 gives the increase in the concentration of tritium in the gas phase at 78° and 90°K at a pressure of 0.1 mm Hg. It can be seen from this figure that the exchange between adsorbed tritium and molecular hydrogen at these temperatures occurs only slowly, and the rate of exchange reduces rapidly with increase in volume thickness. Curves similar in form are obtained for different specimens of film. It is found that the rates of exchange at a single temperature on various samples are in satisfactory agreement. In subsequent experiments on exchange taking place on a single catalyst, in which, during the transition from one experiment to another, the hydrogen is evacuated from the film at 150°C, the rate of exchange steadily diminished. The relative reduction in the rate of exchange was inconsiderable, and usually lay within the limits of experimental error. At 162°K it was not possible to measure the rate of exchange, since adsorption equilibrium was established in less than 30 sec.

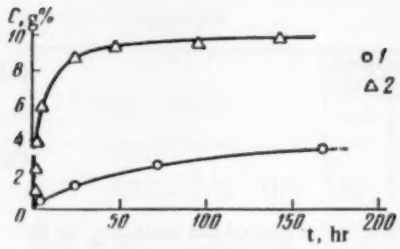


Fig. 4. Increase in tritium concentration in the gas phase: 1) at 78°K (platinum sample No. 10); 2) at 90°K (platinum sample No. 12).

3. Kinetics of the surface exchange. The rate of exchange is suddenly changed with increase in the degree to which exchange takes place between the adsorbed hydrogen and the molecular. This suggests that the surface is inhomogeneous, and, as N. P. Keier [10], S. Z. Roginskii [11] and R. P. Eischens [12] have shown for other systems, the kinetics of exchange of adsorbed particles may be used to elucidate the nature of the inhomogeneity. If this degree of inhomogeneity is sufficiently pronounced, it may be supposed that some portion s of the surface may, at some time during the exchange, arrive at a state of isotopic equilibrium between the adsorbed atoms of hydrogen and the gas phase, while the remaining portion of the surface preserves the initial isotopic composition of the adsorbed hydrogen. In this case, s will determine the degree to which exchange occurs in the adsorbed hydrogen.

We shall use the following notation: C_0 is the initial tritium content in the adsorbed hydrogen; C is the proportion of tritium in the gas; C' is the proportion of tritium in the adsorbed hydrogen on that part of the surface s which is in equilibrium with the gas phase; g_g is the number of hydrogen atoms in the volume; g_a is the number of hydrogen atoms on the surface.

The selectivity of adsorption in relationship to the different hydrogen isotopes is characterized by the adsorption partition coefficient:

$$\alpha = \frac{C'(1-C)}{C(1-C')}. \tag{1}$$

We shall assume that α is uniform for all parts of the surface. From the conservation of the total amount of tritium in the system it follows:

$$g_g C = (C_0 - C')\, s g_a \tag{2}$$

Eliminating C' from (1) and (2) we obtain:

$$s = \frac{g_g C\,[1 + (\alpha - 1)\,C]}{g_a\,[C_0 + (\alpha - 1)\,CC_0 - \alpha C]}. \tag{3}$$

The variation in the degree of exchange with time is then given by:

$$\frac{ds}{dt} = \frac{g_g}{g_a} \frac{[C_0 + 2(\alpha - 1)\,CC_0 + (\alpha - 1)^2 C^2 C_0 - \alpha(\alpha - 1)\,C^2]}{[C_0 + (\alpha - 1)\,CC_0 - \alpha C]^2} \cdot \frac{dC}{dt} \tag{4}$$

4. Determination of α, the adsorption partition coefficient. For the determination of α, the exchange of the adsorbed tritium with hydrogen was carried out in two stages.

The first stage was carried out as described above, but after the attainment of a definite degree of exchange $\underline{s}$, the hydrogen in the reaction space was replaced by pure protium, and the radioactivity in the gas phase again measured. By this means, the second stage of the experiment produced exchange between protium and adsorbed hydrogen, the isotopic composition of which had been the equilibrium value in relation to the gas at the conclusion of the first stage.

If we use the indices 1 and 2 to characterize the course of the exchange during the first and second stages, respectively, we may write, using (3):

$$s_1 = \frac{g_{g_1}}{g_a} \frac{C_1\,[1 + C_1(\alpha - 1)]}{C_{01} + C_{01}C_1(\alpha - 1) - \alpha C_1}; \tag{5}$$

$$s_2 = \frac{g_{g_2}}{g_a} \frac{C_2\,[1 + C_2(\alpha - 1)]}{C_{02} + C_{02}C_2(\alpha - 1) - \alpha C_2}. \tag{6}$$

According to (2), the proportion of tritium in the hydrogen adsorbed on the part of the surface $\underline{s}$, at the beginning of the second stage of exchange, is given by:

$$C_{02} = \frac{\alpha C_k}{1 + C_k(\alpha - 1)}, \tag{7}$$

where C_k is the tritium concentration in the gas at the end of the first stage.

For equal exchange time, $s_1 = s_2$. Hence, taking (7) into account, we find:

$$\alpha = \frac{g}{g_{g_1}} \frac{g_{g_2}}{g_{g_1}} \frac{C_2}{C_1} \frac{[C_{01} + C_{01}C_1(\alpha - 1) - \alpha C_1]\,[1 + C_2(\alpha - 1)]\,[1 + C_k(\alpha - 1)]}{[1 + C_2(\alpha - 1)]\,(C_k - C_2)}. \tag{8}$$

Equating (8) has been used to determine the values of α from the data of a few series of experiments, using different values of $\underline{s}$.

It appears that the value of α does not change significantly with variation in the value of $\underline{s}$. At a temperature of 78°K, $\alpha = 8 \pm 1.7$; and at 90°K, $\alpha = 6 \pm 0.7$.

At low temperatures, the equilibrium constant of the exchange reaction

$$\frac{1}{2}\,T_2 + H[K] \rightleftarrows \frac{1}{2}\,H_2 + T[K],$$

(where K denotes the catalyst surface) is equal to the adsorption partition coefficient, and is obtained from the equation:

$$\alpha = \left(\frac{\nu_{H_2}}{\nu_{T_2}}\right)^{\frac{1}{2}} \frac{\nu_{T[K]}}{\nu_{H[K]}} \cdot e^{-\frac{hC}{2kT}\left[\frac{1}{2}(\nu_{H_2} - \nu_{T_2}) - (\nu_{H[K]} - \nu_{T[K]})\right]} \quad (9)$$

where ν_{H_2}, ν_{T_2}, $\nu_{T[K]}$, $\nu_{H[K]}$ are the oscillation frequencies for molecules of hydrogen and tritium, and adsorbed atoms of tritium and hydrogen respectively; [K] is the catalyst, in this case platinum.

The ratio $\nu_{T[K]}/\nu_{H[K]}$ is equal to the square root of the reduced mass (μ). Since the mass of the hydrogen is much less than that of the platinum,

$$\frac{\mu_{T[K]}}{\mu_{H[K]}} \approx 3 \text{ and } \frac{\nu_{T[K]}}{\nu_{H[K]}} = \sqrt{\frac{1}{3}} = 0.58.$$

Using this ratio, and the experimentally determined values of α, it is possible to calculate from (9) that $\nu_{T[K]} = 1600\ cm^{-1}$, and $\nu_{H[K]} = 2800\ cm^{-1}$.

Since $\nu_{D[K]}/\nu_{H[K]} = (1/2)^{1/2}$, it follows that $\nu_{D[K]} = 2000\ cm^{-1}$.

TABLE 2

The Adsorption Partition Coefficient for the Isotopes of Hydrogen

Exchange reaction	Partition coefficient	
	78°K	90°K
$\frac{1}{2}T_2 + H[K] \rightleftarrows \frac{1}{2}H_2 + T[K]$	8,3	6,0
$\frac{1}{2}D_2 + H[K] \rightleftarrows \frac{1}{2}H_2 + D[K]$	4,6	3,7
$\frac{1}{2}T_2 + D[K] \rightleftarrows \frac{1}{2}D_2 + T[K]$	1,8	1,6

Using the values for the frequencies of the adsorbed atoms found in this way, it is possible to calculate the partition coefficients for the adsorption of H_2 and D_2, and also for D_2 and T_2. The calculated values are shown in Table 2.

5. Activation energy for the exchange between adsorbed and molecular hydrogen. The values of the adsorption partition coefficients which have been found make it possible to calculate the rate of exchange, ds/dt, using Eqs. (3) and (4), for different degrees of exchange (s).

The results are given in Figs. 5 and 6.

It is seen from Fig. 6 that the value of log (ds/dt) initially undergoes rapid reduction with increase in s, and that afterwards, over a considerable interval, the degree of exchange changes in a way which, to a first approximation, can be represented as linear. The slopes of the linear portions at 78°K and 90°K are the same. It may, therefore, be concluded that on a considerable portion of the surface of the platinum film, the activation energy of the exchange process increases linearly with increase in the extent of the exchange:

$$E = 5.2 + 2.1s \text{ kcal/mole},$$

which corresponds to the so-called equilibrium inhomogeneity. For very low degrees of exchange (less than 1%) the activation energy of the exchange process diminishes rapidly. Figure 7 gives the change in the activation energy of the exchange process with the extent of change.

6. Effect of pressure. Figure 8 gives the results of four experiments in which the rate of exchange of adsorbed tritium with molecular hydrogen was studied at 90°K and at pressures of 0.1 and 1.0 mm Hg.

The experiments were carried out successively on the same platinum film. As has been shown earlier, some reduction in the rate of exchange takes place in successive experiments when intermediate desorption of the hydrogen at 150° is carried out. When this reduction is taken into account, it appears that there is no significant influence of pressure on the rate of exchange.

It follows, therefore, that the exchange between hydrogen adsorbed on platinum, and molecular hydrogen, takes place with zero order.

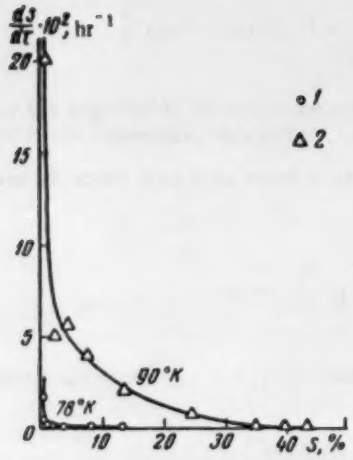


Fig. 5. Relationship between the rate of isotopic exchange for the reaction of adsorbed tritium with molecular hydrogen, and the degree of exchange s. 1) at 78°K (platinum sample 10); 2) at 90°K (platinum sample 12).

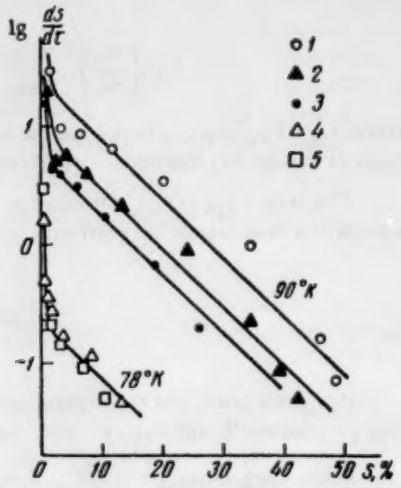


Fig. 6. Relationship between the logarithm of the rate of exchange for the reaction between adsorbed tritium and molecular hydrogen, and the degree of exchange s: 1) at 90°K (platinum sample 12, experiment 1); 2) at 90°K (platinum sample 12, experiment 3); 3) at 90°K (platinum sample 15, experiment 1); 4) at 78°K (platinum sample 10); 5) at 78°K (platinum sample 13).

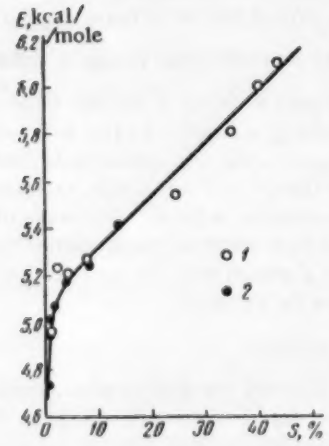


Fig. 7. Relationship between the activation energy for the reaction between adsorbed tritium and molecular hydrogen, and the degree of exchange s: 1) at 78°K (platinum sample 10); 2) at 90°K (platinum sample 12).

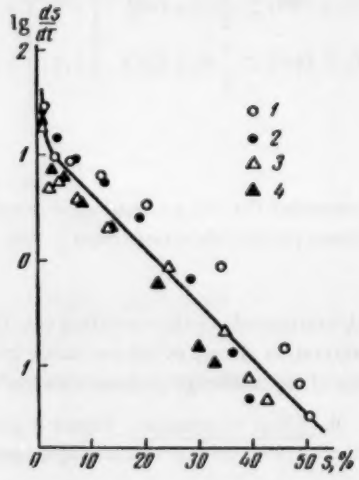


Fig. 8. Relationship between the logarithm of the rate of exchange for the reaction between adsorbed tritium and molecular hydrogen and the degree of exchange, s, at 90° (platinum sample 12): 1) at 0.1 mm Hg (experiment 1); 2) at 1.0 mm Hg (experiment 2); 3) at 0.1 mm Hg (experiment 3); 4) at 1.0 mm Hg (experiment 4).

The Kinetic Isotope Effect

In order to determine the kinetic isotope effects, the rate of exchange has been measured both for the reaction of adsorbed tritium with molecular deuterium, and for that of adsorbed protium with molecular deuterium.

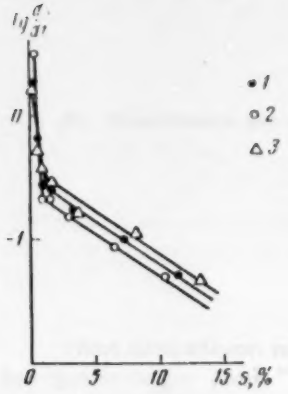


Fig. 9. Relationship of the logarithm of the rate of isotopic exchange to the degree of exchange, s, at 78°K: 1) reaction between adsorbed tritium and deuterium (platinum sample 11, experiment 1); 2) reaction between adsorbed tritium and protium (platinum sample 13); 3) reaction between adsorbed tritium and protium (platinum sample 10).

The first of these reactions was investigated in a manner essentially similar to that used for the reaction between adsorbed tritium and protium. The results of the measurements at 78°K are given in Fig. 9, together with the results for the adsorbed tritium:molecular protium reaction. A comparison of these data shows that the change in the rate of exchange by substituting deuterium for protium lies within the limits of fluctuation for the rate for the same reaction when measured on different platinum films. It follows that the magnitude of the kinetic isotope effect is close to unity.

In the study of the exchange reaction between adsorbed protium and molecular deuterium, the rate of exchange was calculated from the increase in the concentration of protium in the gas phase, measured by the thermal conductivity method. The same tubes, containing platinum wires, as had been used for the study of the exchange reaction between molecular protium and molecular deuterium were used for this purpose, but the calibration of the tubes was carried out by using mixtures of protium and deuterium of various compositions, equilibrium being established between the species H_2, D_2 and HD.

The following is a description of the experimental method: protium was adsorbed on the clean surface of a platinum film, and the excess of protium was evacuated away. The reaction vessel was then shut off. Into the system, and the gas analysis tubes, deuterium was introduced at a pressure of 0.1 mm Hg. The tubes were then disconnected, and the pressure in the system was increased to such a value that, when deuterium was allowed to enter the reaction vessel, its pressure was equal to that in the tubes. After the introduction of the gas into the system, only one of the tubes was connected up, the other being used as a standard tube. The rate of exchange was determined from the deviation of the galvanometer needle from the zero position after a certain time. The conversion of the galvanometer reading into a protium composition was carried out from a calibrating curve.

For the extent of exchange, in this case, we find a relationship similar to (3) when $C_0 = 1$:

$$s = \frac{g_g}{g_a} \frac{C[\alpha - C(\alpha - 1)]}{\alpha(1 - C)}.$$

The results obtained are shown in Fig. 10.

The exchange between adsorbed protium and molecular deuterium takes place about seven times faster than the exchange between adsorbed tritium and molecular protium. Since it has been shown in previous experiments that the rates of exchange of adsorbed tritium with protium and deuterium are identical, then it is possible to conclude from the results obtained that the kinetic isotopic effect of transfer of adsorbed hydrogen into the gas phase, when tritium is replaced by protium, amounts approximately to 7.

As one of us has shown earlier [13], the following relationship exists between the kinetic isotopic effects of the direct and reverse reactions, and the equilibrium partition coefficient:

$$\frac{\alpha}{\beta} = \alpha^{M}.$$

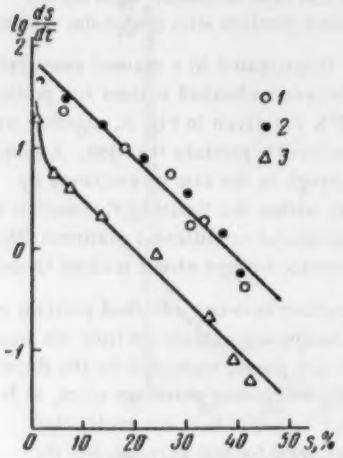


Fig. 10. Relationship between the logarithm of the rate of isotopic exchange and the degree of exchange at 90°K: 1) for the reaction between adsorbed protium and molecular deuterium (platinum sample 11, experiment 2); 2) for the reaction between adsorbed protium and molecular deuterium (platinum sample 14); 3) for the reaction between adsorbed tritium and molecular protium (platinum sample 12, experiment 3).

For the process under consideration, $\vec{\beta}$ is the ratio of the rate of transfer of adsorbed hydrogen into the gas phase for protium and tritium; $\overleftarrow{\beta}$ is the same for the reverse process; α is the partition coefficient of tritium and protium on adsorption; M is the "molecularity" of the reaction, that is, the number of adsorbed atoms of hydrogen transferred into the gas phase on the conversion of one activated complex.

Therefore,

$$\vec{\beta} > 1.$$

Consequently,

$$\vec{\beta} > \alpha^{M}.$$

For 90°K it is found that

$$\vec{\beta} \sim 7 \text{ and } \alpha \sim 6,$$

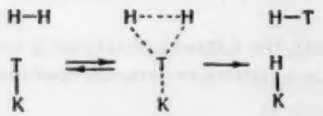
from which it follows clearly that M = 1, that is, the conversion of one active complex leads to the transfer of only one adsorbed hydrogen atom into the gas phase.

Discussion of Results

1. Comparison of the rates of isotopic exchange between molecules of hydrogen, and between adsorbed atoms and molecules. Comparison of the rate of exchange between molecular protium and deuterium at 78°K, with that (under the same conditions) between adsorbed tritium and molecular protium, shows that the latter, even at the beginning of the exchange process, is less than the former by a factor of 1200. For the later experimental points, because of the rapid decline in the rate of exchange between adsorbed hydrogen as the extent of exchange increases, the difference between the rates becomes still greater. A similar relationship between the rates is also observed at 90°K. The observed difference between the rates cannot be explained by the kinetic isotope effect, for this, as we have shown above, is not greater than a factor of 7. It follows, therefore, that at the temperatures at which the investigations have been carried out, the isotopic exchange between molecules of hydrogen takes place without the participation of any appreciable quantity of hydrogen adsorbed on the platinum: that is, the process takes place on only a small fraction (much less than 1%) of the catalyst surface [14].

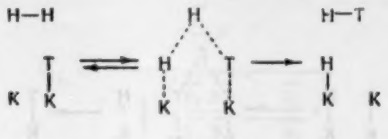
2. The mechanism of the exchange between adsorbed and molecular hydrogen. G. Schuit [4] considers that the following three mechanisms are possible for the catalytic isotopic exhhange with molecular hydrogen:

I. A molecule of hydrogen from the gas phase forms an active complex with an adsorbed atom, the complex occupying the same unit of area as the atom.



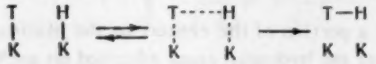
(The Eley-Raidil mechanism I).

II. A molecule of hydrogen from the gas phase reacts with an adsorbed atom which is situated near to unoccupied areas, forming an activated complex which occupies two units of area:



(The Eley-Raidil mechanism II).

III. Simultaneous desorption (and adsorption) of two atoms occurs:



(The Bonhoffer-Farkash mechanism).

These three schemes may also be used to explain the exchange between adsorbed atoms and molecular hydrogen in the gas phase.

Investigations of the adsorption of hydrogen at 78°K and 90°K have shown that under the conditions under which exchange occurs, the number of atoms of adsorbed hydrogen on the surface is approximately equal to the number of platinum atoms. Adsorption of molecular hydrogen in excess of this quantity also takes place, but to a negligible extent.

In connection with these three schemes, the following kinetic characteristics (Table 3) should be taken into consideration.

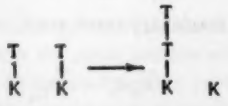
TABLE 3

Scheme for reaction mechanism	Molecularity, M	Order of reaction, n	Change in rate in relationship to the isotopic composition of hydrogen	
			on the surface	in the volume
Eley-Raidil I	1	1	Considerable	Considerable
Eley-Raidil II	1	from $\frac{1}{2}$ to 1	The same	The same
Bonhoffer-Farkash	2	0	The same	Absent
Experimental data	1	0	The same	The same

Comparison of these characteristics with the experimental data shows that none of the three schemes under consideration is in harmony with the results obtained. The adsorption-desorption scheme of Bonhoffer and Farkash agrees with the experimental data with respect to the order of reaction and the effect of isotopic composition, but this scheme gives a wrong value for the molecularity of the reaction. This fact compels us to recognize that the desorption of hydrogen at low temperatures proceeds according to a more complicated scheme.

The value M = 1 found experimentally for the molecularity of the process points to the fact that the two hydrogen atoms are not liberated simultaneously from the surface during desorption.

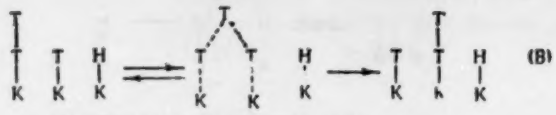
It appears that one atom is liberated first, with the formation of a molecule of hydrogen bonded with the surface (which may, perhaps, be the positively charged ion H_2^+):



(A)

The activation energy of this process for the basic part of the surface varies linearly from 5 to 7 kcal/mole.

The molecule formed remains quite strongly bound to the majority of surface positions, and its transfer into the gas volume requires a considerable activation energy. One of its atoms, however, may be easily transferred, becoming linked with a neighboring hydrogen atom.



(B)

This process, which can be regarded as a special type of diffusion of the hydrogen atoms separating from the surface through the fundamental layer of adsorbed atoms on the surface, needs no significant activation energy, and takes place with a velocity which considerably exceeds the velocity of stage (A).

It has been shown above that a portion of the centers on the platinum film surface are characterized by low exchange activation energy, and the hydrogen atom adsorbed on such centers proceeds rapidly to a state of equilibrium with the gas phase.

When the molecular form of the adsorbed hydrogen, as a result of transfer along the surface, reaches one of these centers, it will then proceed into the gas phase.

The centers on the surface, thus liberated, are then occupied by atoms or molecules of hydrogen from the gas phase. As a result of the successive nature of the reaction which has been indicated, one atom of tritium on the surface is exchanged for one atom of protium, which corresponds to a molecularity of unity.

3. Mechanism of the isotopic exchange in molecular hydrogen. At low temperatures, isotopic exchange in molecular hydrogen takes place on a small fraction of the surface of the platinum film, and the major part of the adsorbed hydrogen plays no part in the process. It is necessary to suppose that this small fraction of the surface corresponds to those centers for which the activation energy of desorption of the hydrogen molecules is small. The process of exchange may then be regarded as taking place in the following fashion.

Protium and deuterium are adsorbed on free centers on the surface in the form of molecules, each occupying one center. The atom of these molecules which is furthest from the surface may then be transferred, forming molecules with one of the neighboring adsorbed atoms. When such a molecule reaches a center with a low desorption activation energy, it may be transferred into the gas phase. As a result of this, the isotopic composition of the molecules changes without the occurrence of dissociative adsorption. By this means, it is possible to explain the low activation energy of the exchange process. The small value of the pre-exponential factor is due to the fact that the proportion of the centers which has a low desorption activation energy for hydrogen is small, and apparently amounts to no more than 10^{-4}-10^{-5}.

We consider a group of identical centers with low desorption activation energy for hydrogen. The following processes may take place on these:

$$(H_2)_g + [K] \rightleftarrows (H_2)_{ads}[K],$$

$$(H_2)_{ads}[K] + [K] \rightleftarrows 2H_{ads}[K].$$

(where K denotes a vacant center). We use the symbols θ_{H_2}, θ_H, and θ_0 to denote the number of centers under consideration occupied by molecules and atoms of hydrogen, or unoccupied, respectively. Then,

$$\theta_{H_2} + \theta_H + \theta_0 = 1.$$

The conditions of the existence of a stationary state are:

$$\vec{k}_1 p \theta_0 = \overleftarrow{k}_1 \theta_{H_2}$$

$$\vec{k}_2 \theta_{H_2} \theta_0 = \overleftarrow{k}_2 \theta_H^2$$

where p is the hydrogen pressure.

Hence,

$$\theta_{H_2} = \frac{\frac{\vec{k}_1}{\overleftarrow{k}_1} p}{1 + \sqrt{\frac{\vec{k}_1 \vec{k}_2}{\overleftarrow{k}_1 \overleftarrow{k}_2} p} + \frac{\vec{k}_1}{\overleftarrow{k}_1} p}$$

$$\theta_H = \frac{\sqrt{\frac{\vec{k}_1 \vec{k}_2}{\overleftarrow{k}_1 \overleftarrow{k}_2} p}}{1 + \sqrt{\frac{\vec{k}_1 \vec{k}_2}{\overleftarrow{k}_1 \overleftarrow{k}_2} p} + \frac{\vec{k}_1}{\overleftarrow{k}_1} p}$$

$$\theta_0 = \frac{1}{1 + \sqrt{\frac{\vec{k}_1 \vec{k}_2}{\overleftarrow{k}_1 \overleftarrow{k}_2} p} + \frac{\vec{k}_1}{\overleftarrow{k}_1} p}$$

Extrapolating the results of the study of adsorption on the portion of the surface under consideration, we may postulate that,

$$\theta_H \gg \theta_{H_2} + \theta_0.$$

Then,

$$\sqrt{\frac{\vec{k}_1 \vec{k}_2}{\overleftarrow{k}_1 \overleftarrow{k}_2} p} \gg 1 + \frac{\vec{k}_1}{\overleftarrow{k}_1} p$$

and,

$$\theta_{H_2} \approx \sqrt{\frac{\vec{k}_1 \overleftarrow{k}_2}{\overleftarrow{k}_1 \vec{k}_2} p}.$$

The rate constant for the exchange process is equal to the rate of desorption of molecular hydrogen:

$$w = \overleftarrow{k}_1 \theta_{H_2} = \overleftarrow{k}_1 \sqrt{\frac{\vec{k}_1 \overleftarrow{k}_2}{\overleftarrow{k}_1 \vec{k}_2} p},$$

that is, it is proportional to the square root of the hydrogen pressure, in agreement with the experimental data.

The mechanism of the low temperature exchange is closely similar to that proposed by Eley and Raidil (II). The difference consists in that the inhomogeneity of the surface at low temperatures is taken into account in the present scheme, which requires the repeated movement of the second hydrogen atom in the adsorbed molecule until it reaches the center with low desorption activation energy.

As the temperature is increased, the exchange mechanism changes, because of the more rapid growth of the rate of desorption of the atomic hydrogen from the main portion of the surface (E = 6 kcal/mole), in comparison with the rate of desorption of the molecular hydrogen from the part of the surface which is active at low temperatures (E = 1.200 kcal/mole). Thus, when the temperature is raised from 78° to 300°K, the ratio of the rates changes by a factor of 10^{10}. If, on the basis of the values of the energies of activation found experimentally, we suppose that the rate of desorption of molecular hydrogen at 78°K is 10^{12} greater than the mean rate of desorption

of atomic hydrogen from the main part of the surface, then on the portion of the surface consisting of active centers, 10^{-5} of the whole, exchange on these will take place with a velocity 10^{7} greater than the rate of exchange on the whole of the remaining part of the platinum surface. At 300°K the rate of desorption of molecular hydrogen from the active centers will be only 100 times greater than the rate of desorption of atomic hydrogen from the remainder of the surface, and the rate of isotopic exchange of the molecular hydrogen on these centers will be less by a factor of 1000 than the total rate of exchange on the remainder of the surface.

Thus, at temperatures higher than 300°K, the exchange with molecular hydrogen on the gas phase will take place on the whole platinum surface, according to an adsorption-desorption mechanism involving dissociation into atoms.

With increase in temperature, a rapid reduction also occurs in the difference between the rates of exchange on the various centers existing on the catalyst surface. Thus, at 500°K, the rate of the exchange reaction over the entire range of the region in which linear variation occurs in the activation energy varies by no more than a factor of 2 or 3.

At high temperatures, therefore, the surface of the platinum film, with respect to the isotopic exchange reaction between adsorbed gas and molecular hydrogen in the gas phase, is practically homogeneous.

SUMMARY

1. Isotopic exchange has been investigated in molecular hydrogen, and also between adsorbed hydrogen on platinum films and gaseous hydrogen. The temperatures used are 78° and 90°K, and deuterium and tritium have been employed in the investigation.

2. The rate of exchange of adsorbed tritium with gaseous protium diminishes rapidly with the degree of completion of the exchange, which indicates inhomogeneity in the surface. The major part of the surface has a gradually varying inhomogeneity, and the activation energy of the exchange process is equal to 5.2 + 2.1s kcal/ /mole. For low degrees of exchange (less than 1%), the activation energy diminishes abruptly. The rate of exchange is independent of the hydrogen pressure.

The partition coefficient for the adsorption of a mixture of tritium and protium has been found to be equal to 6 ± 0.7 at 90°K, and 8 ± 1.7 at 78°K.

An estimate is given of the calculated values of the partition coefficients for other mixtures of the hydrogen isotopes.

The substitution of deuterium for protium in the gas phase does not alter the rate of exchange of the gaseous molecules with adsorbed tritium.

Substitution of protium for the adsorbed tritium (for exchange with gaseous deuterium), increases the rate of the reaction by a factor of 7. By comparing the kinetic isotope effect with the partition coefficient, it has been found that the molecularity of the exchange reaction is equal to unity. A mechanism has been postulated for the isotopic exchange of adsorbed hydrogen with gaseous hydrogen at low temperatures.

3. Isotopic exchange between molecules of hydrogen takes place at 78° and 90°K without the participation of the major part of the hydrogen adsorbed on the platinum: only a small portion of the catalyst surface is active in this process. The order of the reaction is 0.5, and the activation energy is 1.2 kcal/mole. A mechanism has been proposed for the isotopic exchange in molecular hydrogen at low temperatures. At higher temperatures (above 300°K), the exchange takes place practically over the entire platinum surface, according to the adsorption-desorption mechanism proposed by Bonhoffer and Farkash.

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THE NATURE OF THE CHANGE IN HEAT AND ACTIVATION ENERGY OF ADSORPTION WITH INCREASED SURFACE COVERAGE

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An isotopic investigation of gas adsorption on semiconductor and metal contacts showed that the change in heat and activation energy of adsorption with increased surface coverage was mainly influenced by the heterogeneity of the active surface. This heterogeneity of active surfaces of semiconductor contacts was considered to be due to the presence of chemical impurities, which formed charged defects and so disturbed the periodic electron potential on the surface.

Changes in the heat and activation energy of adsorption with increasing surface coverage have been determined experimentally for catalysts belonging to different classes of solids. These changes could be due to heterogeneity of the active surface or to interaction between adsorbed molecules. The individual effect of these two factors must be known before any theory of chemisorption can be developed.

1. The Effect of Heterogeneity and Interaction on Chemisorption

To distinguish between the effects of heterogeneity and interaction on chemisorption, one must consider the state of the molecules being adsorbed in relation to the extent of surface coverage. If successively adsorbed molecules differ in the stability of their bonds with the surface, then the surface is heterogeneous. If adsorption of gas molecules influences the state of previously adsorbed molecules, this is due to interaction. Both effects may occur together.

The state of adsorbed molecules can be studied directly by their spectra, but the technical difficulties encountered have hindered the application of this method for investigation of heterogeneity and interaction effects. Only recently have infrared spectroscopic studies given qualitative indications of the simultaneous effects of heterogeneity and interaction during adsorption of carbon dioxide on palladium [1]. The application of spectroscopic methods to this question is still limited.

The following indirect isotopic methods for studying the roles of interaction and heterogeneity have been developed: isotopic composition of desorbed gas (DIZ method [2]), rate of exchange of labeled adsorbed gas with gas of different isotopic composition (kinetic isotopic methods [3]), rate of desorption of labeled adsorbed gas when the total surface coverage is increased by adsorption of a gas of different isotopic composition (desorption isotopic method [4]) and so on. Kinetic and desorption isotopic methods allow a quantitative investigation of a) the effect of heterogeneity and b) the combined effects of heterogeneity and interaction.

Many catalysts (metals, semiconductors, and insulators) have been shown to be heterogeneous with respect to adsorption of different gases by isotopic methods [5]. The interaction effect has not been investigated so thoroughly, since the desorption isotopic method has only recently been developed [4].

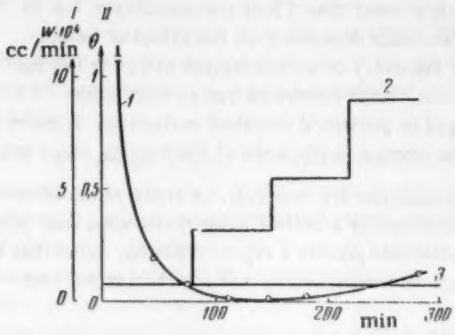

Fig. 1. The effect of interaction on adsorption of acetylene by nickel oxide: 1) rate of desorption of acetylene labeled with C^{14}: T_{ads} = 150°; 2) change in total surface coverage by labeled and ordinary acetylene; 3) change in surface coverage by labeled acetylene.

The effect of interaction has been studied in most detail for adsorption of acetylene on nickel oxide. This is also of interest because nickel oxide is a semiconductor with "little-holed" (p-type) conductivity, and acetylene adsorption is accompanied by changes in the amount and activation energy of electrical conductivity. Results from one of these experiments are given in Fig. 1. The nickel oxide was prepared by decomposition of nickel carbonate at 300° in vacuo and had been degassed at 450°. Its specific surface was 39 m^2/g, determined from krypton adsorption by the BET method. Acetylene, labeled with C^{14} carbon, was adsorbed at 150° until the surface coverage reached 6% of the monolayer. The total surface coverage was increased to 95% of the monolayer by adsorption of ordinary acetylene. For complete coverage it was assumed that each nickel cation on the surface would adsorb one acetylene molecule.

The interaction effect was determined from the change in desorption rate of labeled acetylene during the gradual increase of total surface coverage and the small change in surface coverage by labeled acetylene. It had been shown that the rate and activation energy of the desorption process was independent of the isotopic composition. During the adsorption of ordinary acetylene, exchange can take place between labeled acetylene and that which is adsorbed. On a heterogeneous surface, this can result in an increase in the desorption rate and an apparent interaction effect, linked with the redistribution of labeled acetylene on the surface. The amount of exchange during the adsorption time was checked from the radioactive residue of nonadsorbed acetylene, and the necessary correction was small in every case.

In Fig. 1, curve 1 represents the change in desorption rate of labeled acetylene with time; curve 2 the change in total surface coverage by labeled and ordinary acetylene and curve 3 the surface coverage by acetylene labeled with C^{14}. The desorption rate of labeled acetylene decreases markedly in the first 90 min in spite of the fact that the surface coverage by labeled acetylene hardly changes (curve 3). This desorption rate continues to decrease until the total surface coverage reaches 32% and only after an increase to 55% surface coverage does the desorption rate begin to increase to its final value at 91% coverage. An increase from 6 to 91% total surface coverage increases the desorption rate of labeled acetylene by twice its minimum value. This corresponds to a decrease in the activation energy for desorption of labeled acetylene of 0.5 kcal/mole.

Determination of the dependence of the total desorption rate and the desorption rate of labeled acetylene on temperature, when $\Theta_{lab} = 0.06$ and $\Theta_{total} = 0.91$ initially, showed that the activation energies (determined from the changes in desorption rates) differed by a factor of two.

Figure 2 shows the dependence of the logarithm of the total desorption rate (line 1) and desorption of initially adsorbed labeled acetylene (line 2) on the reciprocal of absolute temperature. From the gradients of these lines, the average activation energy for the total desorption process is 9.2 kcal/mole, and the desorption activation energy for the initially adsorbed labeled acetylene is 18.4 kcal/mole. This difference in desorption activation energies for acetylene, which had been adsorbed at high and low surface coverages, can only be due to the heterogeneity of the surface. On a homogeneous surface, the activation energies would be the same.

The change in desorption activation energy of 0.5 kcal/mole due to the interaction effect when the surface coverage approximates to the monolayer is only a fraction of the change in desorption activation energy due to heterogeneity of the active surface.

A comparison of these values shows that until the surface coverage approximates to the monolayer value, the chief reason for the changes in heat and activation energy of acetylene adsorption with increasing surface coverage is the heterogeneity of the active surface.

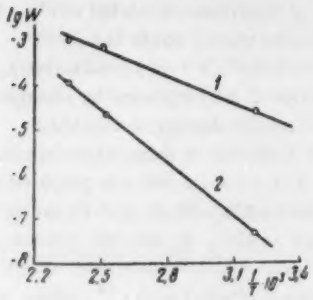

Fig. 2. Relation between log desorption rate and the reciprocal of the absolute temperature: 1) total desorption rate at surface coverage $\Theta = 0.91$ at $T_{ads} = 150°$; 2) desorption rate of labeled acetylene adsorbed initially at $T_{ads} = 150°$ and coverage $\Theta_{lab} = 0.06$.

At metallic nickel contacts the interaction effect exists at a surface coverage lower than 1% of the monolayer, but in this case it also decreases depending on the effect of heterogeneity [6]. This discovery of an interaction effect at low surface coverage means that it cannot be due to coulombic repulsion of charged or polarized adsorbed molecules. A more likely reason is the change in the work of discharging electrons.

Acetylene molecules are nonpolar. A study of the interaction effect on chemically adsorbed polar molecules, like ethyl alcohol, whose molecules possess a dipole moment, shows that in this case the effects of heterogeneity and interaction are commensurate [7].

Isotopic investigation of the effect of heterogeneity on adsorption of hydrogen and acetylene on metallic nickel and copper [8], carbon dioxide on an iron catalyst [9], HCl and H_2 on a tungsten film [10, 11], hydrogen on platinum [12] showed that in all these cases the active surfaces were heterogeneous. Analogous results were obtained for the semiconductor oxide catalysts ZnO, NiO, Al_2O_3 and others [13, 5].

2. Changes in Heat and Activation Energy of Adsorption in the Electronic Theory of Chemisorption

The electronic theory of chemisorption on semiconductors [14] and metals [15] considers the interaction of a solid body with the adsorbed molecule and the resulting redistribution of electrons between the chemisorbed molecule and the solid body. Such an approach can relate the nature of the effect of the electronic structures of the solid body and the molecules being adsorbed with adsorption properties.

Formation of different types of bonds (with transitions between them [14]) between the adsorbed molecules and the surface has been shown possible. In some cases chemisorption solely of charged particles through a sharing of free electrons and holes of the solid body have been examined [16, 17]. The decrease in the heat of adsorption with increasing surface coverage in all the investigations has been linked with the change in potential of the surface due to the formation of a conduction band, equal but opposite in sign to the charge of the adsorbed molecules on the surface. The change in potential of the surface, due to a change in the Fermi level, results in a change in the stability of the bonds of all the molecules previously adsorbed. This kind of change in the heat of adsorption shows up the interaction effect.

These ideas have gained great popularity in the last few years. The change in the work of discharging electrons and electrical conductivity during chemisorption is often considered as indicating the initiation of the interaction effect. But the work of discharging electrons and the electrical conductivity should change during adsorption on both heterogeneous and homogeneous surfaces, therefore by themselves these changes cannot be indicative of the interaction effect alone.

Thus, the chief conclusion from the electronic theory of chemisorption about the reasons for the changes in heat and activation energy of adsorption with increased surface coverage contradicts the results of the relative effects of interaction and heterogeneity by isotopic methods.

We considered that this contradiction could be eliminated by calculating the changes in potential along the surface and in the appearance of adsorption conditions, which are differentiated by the position of the levels relative to the valence band. In this case the appearance of a conduction band and a curved distortion zone displaces all the surface conditions to the same extent, so leaving intact the heterogeneity. If the displacement due to the influence of the conductance band is greater in magnitude than the distance between the adsorption levels, the main effect will be interaction, but if it is less, the main effect will be heterogeneity.

3. Heterogeneity of Semiconductor Contacts

One would expect from the electronic theory of chemisorption a correlation between the adsorption properties of semiconductors and their electronic structure. An interesting case is that of the adsorption properties of impure semiconductors, whose conductivity can be varied over a wide range by formation of chemical defects in their lattices.

An isotopic study of adsorption on nickel and zinc oxides showed that heterogeneity of the active surfaces was the main influence on the change in heat and activation energy of adsorption with increasing surface coverage. In studying adsorption on prepared nickel and zinc oxides, whose electrical conductivities are changed on addition of chemical impurities, the chemical impurity was found to have a strong influence on the heterogeneous nature of the surface in relation to adsorption activation energies. These impurities were added by dissolving oxides of different metals into the semiconductor crystal lattice. The effect of the impurity on the electrical conductivity gave some idea of the nature of the defects which were formed. Only chemical impurities which formed charged defects in the crystal lattice had any effect on the heterogeneity of the active surface.

We will consider the effect of charged defects on adsorption properties for nickel oxide in more detail.

The nickel oxide lattice is built up of Ni^{2+} cations and O^{2-} anions. Its electrical conductivity is determined by the presence of impurities which form or destroy acceptor levels in the electronic zone of the semiconductor scheme. The impurity acceptor levels are formed when cations with reduced valency are introduced into the crystal lattice, and in the same way when cationic holes are formed in the presence of oxygen in excess of the stoichiometric ratio. The electrical neutrality of the crystal is maintained by formation of equivalent amounts of Ni^{3+} cations, which are associated at low temperature by coulombic interaction with the excess negatively charged oxygen ions in the vicinity of cationic holes or sites occupied by univalent cations, for example Li^{+}. With increasing temperature a Ni^{3+} cation can break away from a Li^{+} cation and become free. This corresponds to the formation of a hole in the valence band. The free Ni^{3+} cation can move about in the lattice, thus providing electrical conductivity. The Li^{+} cation, after this breaking-away process, forms a negative hole. Both the Ni^{3+} cation and the negative hole upset the periodic electron potential of the surface and locally polarize the lattice. In contrast to the mobile Ni^{3+} cations, negative holes bring about a steady change in potential of the surface, which is linked with the distribution of the impurity in the surface and near-surface layers. Since coulombic interactions diminish slowly with distance, negative holes situated 6-7 crystal planes below the surface influence the potential of electrons in cationic units on the surface.

Adsorption of electron-donor and electron-acceptor gases has been studied on nickel oxide and on its solid solutions with Li_2O and Fe_2O_3 [5, 18]. The lithium concentration in nickel oxide was varied from 0.1 to 8 atm%. Oxygen and carbon monoxide are electron-acceptor gases, and their adsorption is accompanied by a decrease in electrical conductivity, indicating that the adsorbed molecules become negatively charged. Acetylene and carbon dioxide become positively charged on adsorption, and decrease the electrical conductivity. A 0.2 to 0.4 atm % lithium content exerts a strong but opposite effect on adsorption of both electron-acceptor and electron-donor gases. The adsorption rate of electron acceptors, oxygen and carbon monoxide, is increased; the amount of adsorbed gas in a pseudoequilibrium state increases. The adsorption rate of electron donors, acetylene and carbon dioxide, is decreased, and adsorption ceases completely at lithium contents of 0.4 to 0.5 atom % in NiO [18]. A solution of ferric oxide in NiO has a reverse effect, in that the adsorption rate decreases sharply.

Figure 3 contains kinetic adsorption isotherms for oxygen on solid solutions of nickel oxide with varying lithium and iron concentrations. The kind of relationship between the change in adsorption rate and the extent of surface coverage of the solid solutions, containing different concentrations of defects, is very interesting. Figure 4 shows the change in initial adsorption rate, where this rate is seen to increase sharply (in relation to the case of the original nickel oxide) at low surface coverage for lithium content 0.2 at. %, and to increase slightly on further increase of the lithium concentration to 0.8 at. %. At higher contents (8 at. %) the initial adsorption rate decreases, approaching the rate for nickel oxide. Solutions of ferric oxide strongly decrease the initial adsorption rate. The lithium concentration not only affects the initial rate but also the way in which the adsorption rate decreases with increasing surface coverage; the higher the lithium concentration, the more slowly the adsorption rate decreases with increasing surface coverage. This change in adsorption rate corresponds to a change in the activation energy (Fig. 5). Introduction of 0.2 at. % lithium reduces the activation energy at initial surface coverage from 30 to 10 kcal/mole. Further increase in lithium concentration to 0.4 at. % only affects the gradient

of the line, which becomes less steep. Introduction of ferric oxide displaces the straight line relation between E and q towards lower values of surface coverage. Oxygen adsorption on the original nickel oxide proceeds with time according to:

$$q = At^{\frac{1}{n}} \tag{1}$$

and on solid solutions with lithium oxide according to:

$$q = B \lg t + C. \tag{2}$$

No change in the adsorption kinetics occurs on increasing the lithium concentration from 0.2 to 8 at. %. From the observed adsorption kinetics on a heterogeneous surface there is a relation between the exponential distribution function of active centers and the adsorption activation energies, which for the oxide is:

$$p(E) = He^{\alpha E}, \tag{3}$$

and for solid solutions of nickel oxide with a constant amount of lithium oxide:

$$p(E) = H = \text{const}. \tag{4}$$

The value of H increases with increasing lithium content. The amount of adsorption depends on the kind of distribution function and the minimum value of the adsorption activation energy. Figure 4 shows that the initial adsorption rate hardly changes between lithium concentrations 0.2 to 0.8 at. %, but decreases on increasing the

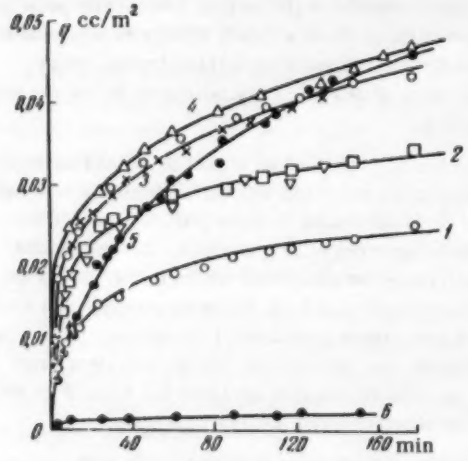

Fig. 3. Kinetic adsorption isotherms for oxygen on NiO and its solid solutions with Li_2O and Fe_2O_3 at T_{ads} = 153°: 1) NiO; 2) NiO (0.2 at. % Li); 3) NiO (0.4 at. % Li); 4) NiO (0.8 at. % Li); 5) NiO (8 at. % Li): 6) NiO (1 at. % Fe).

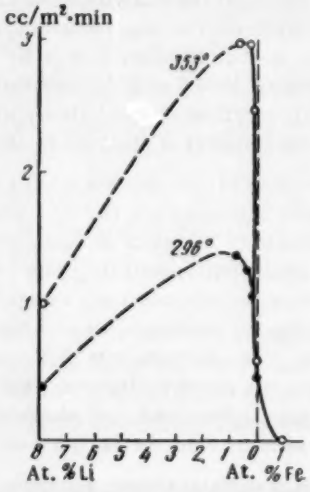

Fig. 4. Change in initial adsorption rate for oxygen on NiO and its solid solution in relation to the cationic concentration of Li^+ and Fe^{3+} at T_{ads} = 153°.

concentration to 8 at. %. This sort of variation of adsorption rate is connected with an increase in the minimum adsorption activation energy on increasing lithium concentration. This activation energy increases from 10 to 16 kcal/mole for an increase in the lithium concentration of 0.2 to 8 at. %, and the increase is linked with the reciprocal effect of the impurity, which also results in a decrease in the electrical conductivity activation energy from 20 to 10 kcal/mole. A solution of ferric oxide decreases the value of H in Eq. 3.

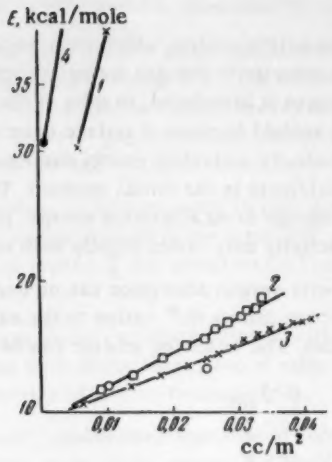

Fig. 5. Change in activation energy for adsorption of oxygen on NiO and its solid solutions with Li_2O and Fe_2O_3; 1) NiO; 2) NiO (0.2 at. % Ni); 3) NiO (0.4 at. % Li); 4) NiO (1 at. % Fe).

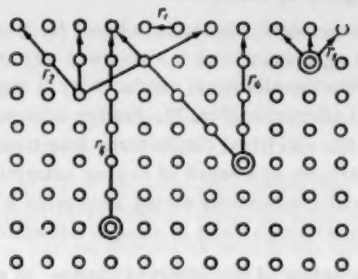

Fig. 6. Heterogeneity in distribution of Ni^{2+} cations according to their distance from Li^+ cations.

We will consider the way in which the defects affect the adsorption properties of nickel oxide. Studies on the electrical conductivity of nickel oxide showed clearly that the positive holes are responsible for the conductivity and not the free electrons. Oxygen adsorption increases the electrical conductivity, confirming an increase in the concentration of Ni^{3+} cations. It is therefore assumed that oxygen adsorption proceeds by interaction of oxygen molecules with Ni^{2+} cations. Ni^{2+} cations on the surface are heterodynamic. Ni^{2+} cations discharged from negative holes at such a distance that they do not interact with them correspond to electrons in the valence band. The electron potential will be lower at these cations than at Ni^{2+} cations which are near negative holes, which correspond to electrons in the localized acceptor levels. Cations which are 2-3 cationic units away from a negative hole will have an intermediate electron potential: the higher the electron potential, the higher the heat of adsorption of electron-acceptor gases, and consequently the lower the adsorption activation energy and the easier the adsorption process on these Ni^{2+} cations. Heterogeneity of the surface is determined by the distribution of Ni^{2+} cations on the surface with respect to their distance from foreign cations which form negative holes (Fig. 6). This model of active centers shows that the distribution function must increase with increasing concentration of foreign cations which form negative holes. This relationship was observed experimentally.

The observed dependence of adsorption on temperature is also important in these considerations [5].

The probability of formation of negative holes is higher, the lower the interaction energy between Ni^{3+} cations and excess negative holes. This value also determines the electrical conductivity activation energy. The equilibrium amount of negative holes depends on temperature according to:

$$N = \sqrt{C[A]}\, e^{-E_\sigma/2RT}, \qquad (5)$$

where [A] is the concentration of acceptor impurity and E_σ is the electrical conductivity activation energy.

If the distribution of Ni^{2+} cations on the surface according to the adsorption activation energy near a defect is denoted as $n(E_{ads})$, the total distribution of active adsorption centers will be of the form:

$$D(E_{ads}) = \sqrt{C[A]}\, e^{-E_\sigma/2RT} n(E_{ads}) = H(T)\, n(E_{ads}), \qquad (6)$$

i.e., the distribution function must depend on temperature since the concentration of negative holes increases with temperature.

This relation is confirmed experimentally. The distribution function of active centers is found to depend on temperature for adsorption of oxygen and acetylene on nickel oxide. For nickel oxide, H is changed in Eq. 3 with activation energies less than E_σ as a result of the strong change in it at the moment the oxygen is introduced.

For adsorption of oxygen on NiO (8 at. % Li) H varies with the activation energy E_σ, since in this case E_σ is affected slightly by adsorption.

The proposed adsorption scheme for an electron-acceptor gas on active centers, which form negative holes, is in good agreement with the observed way in which the electrical conductivity changes during adsorption. On nickel oxide the electrical conductivity is doubled at the moment oxygen is introduced, in spite of the very small amount of adsorption (Fig. 7). Further adsorption has little effect. A tenfold increase of surface coverage only increases the electrical conductivity four times. The electrical conductivity activation energy decreases from 34 to 16 kcal/mole as a result of oxygen adsorption, decreasing to 10 kcal/mole in the initial moment. The increase in electrical conductivity during adsorption is linked solely with the change in its activation energy. In the presence of lithium, although there is stronger adsorption, the electrical conductivity only varies slightly with adsorption.

The nature of this observed change in electrical conductivity with oxygen adsorption can be explained if it is assumed that Ni^{3+} cation formed as a result of transfering an electron from a Ni^{2+} cation to the adsorbed atom or molecule of oxygen, remains in association with the adsorbed species. The following scheme can be proposed:

$$\begin{bmatrix} Ni^{2+} & Li^{+} & Ni^{2+} \\ O^{2-} & O^{2-} & O^{2-} \end{bmatrix} + O_2 - \cdot \begin{bmatrix} Ni^{2+} & Li^{+} & Ni^{3+} \\ O^{2-} & O^{2-} & O^{2-} \end{bmatrix} (O_2)^{-}_{ads}.$$

But this would not bring about a change in the electrical conductivity. However, the localized acceptor level, formed as a result of adsorption, will be situated lower than before adsorption, i.e., nearer the valence band, and so the stability of the bond of a Ni^{3+} cation near a Li^{+} cation will be decreased, since the Ni^{3+} cation, formed as a result of adsorption and associated with the adsorbed molecule, partly compensates the charge of the negative hole. The fraction of acceptor levels occupied by electrons as a result of adsorption will be higher than for the initial acceptor levels. So in spite of the fact that the Ni^{3+} cation formed remains associated with the negatively charged adsorbed molecule, the surface as a whole has an excess negative charge, considerably lower than the charge of the adsorbed negatively charged molecules. The compensating positive charge in the form of a concentration excess of Ni^{3+} cations or holes in the layers near the surface sets up a diffusion potential V_d, which results in an upward distortion of the energy zones near the surface. This distortion leads to a lowering of the Fermi level at the surface and an increase in the work of discharging electrons. A change in the work of discharging electrons is due to formation of dipoles during adsorption and displacement of the Fermi level at the surface as a result of the curved distortion zone, which is determined by the change in position of local acceptor levels during adsorption. For this reason there is no correlation between the change in the work of discharging electrons and the amount of oxygen adsorbed on NiO and its solid solutions with Li_2O. The marked effect of the initial, small amounts of adsorbed oxygen on the activation energy of electrical conductivity is connected with surface heterogeneity. Initial adsorption of Ni^{2+} cations near Li^{+} or cationic holes must result in the most marked change in position of localized levels, which occurs experimentally.

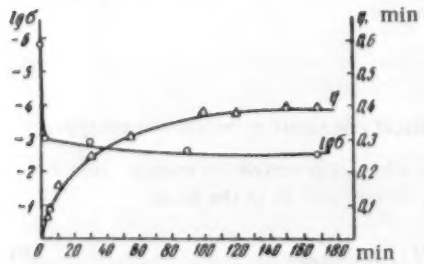

Fig. 7. Change in electrical conductivity during adsorption of oxygen on NiO; T_{ads} = 23°.

The greater the distance between a Ni^{2+} cation on the surface and a negatively charged defect, the weaker the adsorption effect on the position of the localized acceptor level, the weaker the disturbance of the equilibrium distribution of electrons between the valence zone and the acceptor level, and the weaker the adsorption effect on electrical conductivity. The initial position of the localized acceptor level, which is dependent on the chemical nature of the impurity introduced, affects the magnitude of the change in it during adsorption — the higher the level, the greater the decrease. The distribution function $n(E_{ads})$ in Eq. (6) not only depends on the distribution of Ni^{2+} cations on the surface in relation to positive and negative holes, but also on the nature of the change in localized acceptor levels resulting from adsorption.

Negative holes have the reverse effect on the adsorption capacity of free Ni^{3+} cations, which themselves have a low electron potential and are therefore centers for adsorption of

donor gases. Ni^{3+} cations, associated by coulombic interaction with negative holes, lose their activity.

Solution of trivalent metal oxides lowers the electrical conductivity of nickel oxide. Simultaneous solution of equal amounts of lithium and ferric oxides does not change the conductivity. Trivalent ferric cations, in the neighborhood of a lithium cation, destroy negative holes. On solution of ferric oxide in nickel oxide, the adsorption of electron-acceptor gases decreases abruptly. Adsorption of electron-donor gases is decreased slightly, since the concentration of Ni^{3+} cations, which form the active adsorption centers, is decreased.

A solution of lithium oxide in zinc oxide exerts an analogous effect on the adsorption properties, since negative holes are formed in the same way. Solution of lithium oxide in Cu_2O has no effect on adsorption properties, since in replacing the univalent Cu^+ cation with a univalent Li^+ cation, a negative hole is not formed (Kutseva's results).

Heterogeneity can also be linked with crystal structure; with the presence of crystallographic planes which differ in the work of discharge, and of other structural defects. These factors apparently play a less important role in the formation of surface heterogeneity.

Recently papers have appeared in connection with the electronic theory of chemisorption, in which the heterogeneity of an active surface has been studied by summing the adsorption on different activated centers [19-21]. These investigations do not link the heterogeneity with any assumptions about a model. Heterogeneity does not affect the form of equilibrium isotherms, since the basic effect is that of interaction.

Isotopic results show that the active surfaces of metal catalysts are also heterogeneous. Experimental results indicate the strong influence of chemical impurities on adsorption and catalytic properties, but in this case the mechanism of this influence is less clear.

SUMMARY

1. The basic effect on the change in heat and activation energy of adsorption of nonpolar molecules on different contacts with increasing surface coverage is due to heterogeneity of the active surface. Until monolayer coverage is approached, the interaction effect is small compared to this.

2. Heterogeneity of the active surfaces of semiconductor catalysts is linked with the effect of positively and negatively charged holes, which change the electronic potential at the surface, and are formed on introduction of chemical impurities.

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THE CATALYTIC FUNCTION OF METAL IONS IN A HOMOGENEOUS MEDIUM

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The various catalytic systems, containing metal ions, are described in this paper. The systems are classified on a structural basis: the simplest system is ion exciting a chain reaction; more complex is ion–substrate; still more complex systems are ion – carrier – substrate, complex ion – substrate, complex ion – carrier – substrate.

Examples of each class of catalytic systems are described, and original material is presented to illustrate the characteristic features of their action.

Transition metal ions, showing variable valency, behave as active catalysts for a very wide range of chemical transformations.

There is now evidence to show that metal ions can function as catalysts for processes of hydrogenation by molecular hydrogen, decarboxylation, bicarbonate decomposition, hydrolysis, etc.

Catalytic properties are not only shown by transition metal ions, but also by potassium and sodium ions, which behave like hydrogen ions and can, for example, accelerate condensation processes in a homogeneous medium [1].

Metal ions can act as activators for a number of ferments [2], such as aminopeptidase (manganese and magnesium). They can also form highly active complexes, and, as such, can enter into the composition of the active groups of a number of ferments.

We propose, in this paper, to systematize the main forms of catalytic action of metal ions and to describe methods of activating them, so as to increase their activity and create systems which can be considered as ferment models.

The simplest mode of action of a variable valency ion is the initiation of a radical chain reaction. An example of this is the action of the cobalt ion in benzaldehyde oxidation. Here, the change in ion charge leads to the formation of free radicals. A large number of examples, illustrating this type of ionic action, can be found in the work of N. N. Semenov, N. M. Émanuél, and their co-workers [3]. It is obvious that the character of the reaction is determined, to a considerable extent, by the nature of the radical formed.

The second catalytic mode of action of an ion is based on formation of a metal ion – substrate complex. These complexes are usually more or less labile, but their existence can be revealed by physicochemical methods such as spectrophotometry. It is convenient to classify these complexes into two groups. The first group comprises those complexes within which there is electron transfer between ion and substrate in the catalytic process, with the change in ionic charge being an important stage in the catalytic reaction. An example is catalysis of ascorbic acid oxidation by copper ions. The second group comprises reactions where the catalytic ion is of constant valency. In particular, the decarboxylation of keto acids – carboxycarbonylsuccinic acid, carboxycarbonylacetic acid, but not acetoacetic acid – is accelerated not only by salts of copper and iron, but also by salts of zinc, aluminum, and, to a lesser extent, by salts of calcium, barium, and magnesium [4]. Kornberg [5] investigated the catalytic

properties of the aluminum ion in this reaction by spectrophotometric means. He established that aluminum formed very unstable complexes with carboxycarbonylsuccinic and carboxycarbonylacetic acids. These complexes were of a chelate nature, and the mechanism of the action of the aluminum ion was obviously based on the powerful polarizing action which the ion exerted on the keto acid anion.

A more complicated case occurs when the metal ion shows catalytic properties in a system consisting of substrate, ion, and some third constituent, which participates in the reaction by some means or other. This third component may be called a "carrier." The ion forms a labile complex, of the chelate type, with the carrier. In this complex there is a free space in the coordination sphere of the ion; the space is occupied by a substrate molecule at the time of reaction. A typical example of this is the activation of aminopolypeptidase by manganese and magnesium ions. The same principle evidently applies to the action of the copper ion in metalloflavoproteins, which catalyze hydrogen transfer.

A. Gudo considered a different case of interaction in the system protein – metal – substrate [6], and noted the following special features.

The oxidation-reduction potential of the system cation – polarized substrate molecule must be high enough for the substrate to be oxidized; it is necessary that the number of donor groups should correspond to the number of electrons acceptable by the metal ion. This second condition explains the failure of attempts to decarboxylate carboxycarbonylacetic acid with the aid of free magnesium ion. In fact, this cation gives octahedral complexes with three molecules of the above acid, but only requires two electrons to become neutralized. In this case, there is no possibility of catalytic reaction between the divalent metal ion and three substrate molecules.

The third type of active combination, including a metal ion, comprises those complexes in which the increased activity of the ion is achieved by association with a definite addendum, which is not the reaction substrate. The classical example of this type of complex is provided by the metalloporphyrins. The copper-amine complexes show high activity in oxidation-reduction reactions. From Gudo's point of view, electron transfer from metal to substrate is characteristic of catalysis by metal ions.

It should be noted that in spite of the undoubted applicability of this conception to catalysis by simple ions, the reasons for the very high activities of certain complexes remain unknown, and it is not clear why the change in charge of a copper ion does not lead to the development of the normal chain, characteristic of the action of a simple ion. We have shown that there is a difference in mechanism between the actions of simple and complex ions; the active complex ions do not give chains, but form intermediate products. It is also difficult to explain the constancy of activation energy in catalysis by copper complexes and the peculiar response of complexes to activation by means of adsorption. All this suggests that the catalytic function of complex ions differs from that of simple ions [7].

A still more complicated system is that in which a high activity is achieved by combination of a metal-addendum complex with a protein carrier. Representative of this class are ferments and their "models," some of which we have investigated.

Given below are the results of investigation of various catalytic systems containing metal ions. These are considered in accordance with the above classification, i.e., in order of increasing complexity, beginning with systems in which the redox process is the main catalytic stage.

Oxidation of ascorbic acid, in the absence of oxygen but with Methylene Blue as a hydrogen acceptor, deserved investigation, since the dehydrogenating function of metal ions is revealed by this reaction.

1. Redox Processes in the System Metal Ion – Substrate

For a long time, the dehydrogenating action of metal ions did not excite the attention of experimentalists, who considered that the existence of the appropriate difference in value of the redox potential often made careful selection of the catalyst unnecessary. It often escaped attention that a very small number of catalysts actually took part in well-known reactions.

As we have already mentioned, it was only recently discovered that copper is a constituent of certain flavoproteins. G. Mahler [8] showed that precisely these flavoproteins (dehydrogenase butyryl coenzyme A) were capable of oxidizing cytochromes, i.e., they formed the main link in the chain of oxidation-reduction transformations leading to hydrogen transfer from the substance being oxidized to oxygen. This author considered that the

metal increased the stability of the intermediate semiquinone and provided a bond between flavin and acceptor, facilitating electron transfer within the limits of a single complex.

We investigated whether metal ions acted in a similar way in simpler systems, such as mixtures of ascorbic acid or cysteine(hydrogen donors) with Methylene Blue (hydrogen acceptor). The course of the reaction could be followed conveniently by the change in color of the dye; moreover, the dye readily catalyzed ascorbic acid oxidation in the presence of oxygen, since its reduced form was easily oxidized by oxygen. The rate of oxygen absorption could, therefore, also be used as a measure of the intensity of hydrogen transfer [9]. Decolorization of Methylene Blue by ascorbic acid took place rapidly in the light, but slowly in the dark.

Cysteine behaved in a similar way, but the reaction rate was considerably less, both in the light and in the dark.

In order to find out whether metal salt impurities were acting as accelerators to this reaction, we added to the Methylene Blue solution substances which formed stable, inactive, and poorly soluble complexes with heavy metal ions. For this purpose, we used trilon (the sodium salt of ethylenediaminetetraacetic acid) of cupferron, both of which give complexes having no catalytic activity.

Method of Investigation

The rate of formation of the leuco form of Methylene Blue was investigated using a spectrophotometer with automatic recording (SF-2M). The solutions of Methylene Blue and ascorbic acid were placed in a plexiglas cell, fitted with a movable partition. The partition could easily be removed from its groove and replaced after mixing the liquids. This type of cell made it possible to record the absorption spectrum of the solutions of Methylene Blue and ascorbic acid (or any other reducing agent) when the solutions were separated by the partition, and then again after mixing, so that any errors associated with measuring out the solutions, transferring them to the cell, etc., were automatically avoided.* Monochromatic light was used in our experiments, the wavelength corresponding to the absorption maximum of the dye. The following technique was used for following the reaction in the dark.

The solutions were introduced, one after the other, into the normal type of cell, which was enclosed in a black case provided with a narrow vertical tube, through the top of which fitted the tip of a burette. The mixture was allowed to stand in the dark for a definite time, and then the optical density was determined rapidly (in 2 sec), using a wavelength corresponding to the absorption maximum of Methylene Blue.

The experimental technique has been described previously [10] with reference to acceleration of polyphenol oxidation, hydrogen peroxide decomposition, and Indigo-Carmine oxidation.

Results Obtained

Experiments showed that addition of trilon or cupferron to the Methylene Blue greatly retarded the rate of decolorization of the dye by ascorbic acid (Fig. 1, 2), and the retardation occurred in the light and in the dark. This indicated that the reaction of hydrogen transfer from ascorbic acid to Methylene Blue was catalyzed by traces of metals present in the dye.

It was then necessary to find out which metals accelerated the hydrogen transfer reaction. We therefore tried to accelerate the reaction between Methylene Blue and ascorbic acid by adding salts of different metals. Salts of aluminum, sodium, magnesium, copper, iron, cobalt, nickel, titanium, and chromium were tested. A significant acceleration was only observed in the presence of copper. Figure 2 shows that acceleration then ensued, after a short induction period lasting about two minutes. There was a slight retardation during the induction period, and then the reaction was speeded up, going to almost complete decolorization of the solution. There was no detectable change in the absorption spectrum of Methylene Blue in the visible region when copper was added. The pH of the solution was 2.8 and did not change appreciably during the experiment. Thus, copper can catalyze hydrogen transfer , not only in the metalloflavoproteins, but in much less complicated systems, accounting for effects which have usually been attributed to direct interaction between oxidizing and reducing agents.

*When using this cell, it was necessary to make preliminary measurements to ensure that the dye solutions obeyed the Beer-Lambert law.

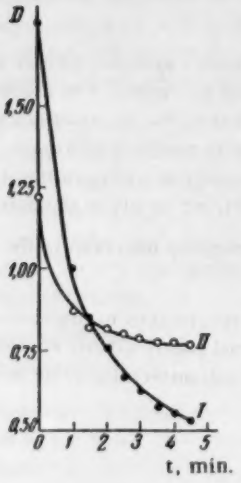

Fig. 1. The retarding action of trilon (1 mg) on the reduction of Methylene Blue (C = 8 mg/liter) by ascorbic acid (C = 5 g/liter) at 25°. The ordinate is the optical density of the solution. I) Change in optical density without trilon, II) with trilon. Reaction in the light; mixture volume 10 ml.

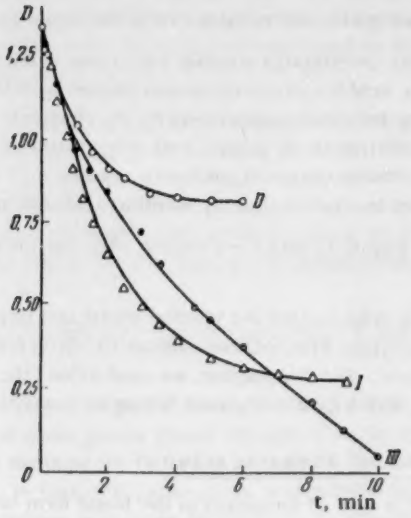

Fig. 2. The effect of cupferron and copper ions on the rate of reduction of Methylene Blue at 25°. I) Decolorization of Methylene Blue by ascorbic acid without additive; II) the same + + 1 mg cupferron; III) the same as I + 0.048 mg copper. The Methylene Blue and ascorbic acid concentration were the same as in Fig. 1.

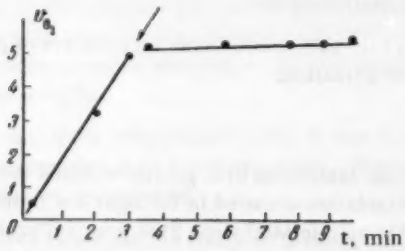

Fig. 3. Catalysis of the oxidation of ascorbic acid by Methylene Blue at 25° (the ordinate is the volume of oxygen absorbed, cm^3). The mixture was 20 ml of Methylene Blue solution (160 mg/liter) in 0.5% ascorbic acid + 1 ml of 15% ammonia. The arrow shows the moment when trilon (0.1 g) was added.

Retardation of the reduction of Methylene Blue by ascorbic acid in the presence of trilon shows that trilon is a "poison" for catalysis of the process of oxidation of ascorbic acid by the dye. Figure 3 shows the course of oxygen absorption by ascorbic acid solution in the presence of a saturated solution of Methylene Blue. It is clear, from Fig. 3, that the reaction rate was almost zero after addition of trilon. We suggest that the first stage in the reaction was the reduction of copper to the univalent state by ascorbic acid. The univalent copper ion then reduced the Methylene Blue.

Retardation by trilon and acceleration by addition of small amounts of copper salts was also observed in the reduction of Methylene Blue by cysteine.

In experiments with cysteine, at pH 3.15, we observed that as little as 3×10^{-5} g-ion/liter of copper accelerated the decolorization reaction by a factor of four (in these experiments the solution was illuminated by a 500 watt lamp, 40 cm away; the cysteine concentration was 1.5 mg/liter). In the experiments with ascorbic acid, the effective copper ion concentration was about 5×10^{-5} g-ion/liter.

The mechanism for ascorbic acid oxidation, proposed by Weissberger and his co-workers [11], where the catalyst is the divalent copper ion, supposes that the acid anion reacts with the divalent copper cation and that, in the resulting chelate complex, there is an electron transfer from an oxygen atom to the copper ion, so that the latter becomes univalent. Dissociation then ensues, since univalent copper gives a less stable chelate complex.

Finally, the ascorbic acid ion radical transforms into dehydroascorbic acid, giving up an electron to a hydrogen ion, which then combines with oxygen to form an HO_2 radical. The HO_2 radical and a univalent copper ion form a divalent copper ion and a hydrogen peroxide anion HO_2^-. In the decolorization reaction, the role of oxygen is fulfilled by the dye, which adds on an electron and proton, while water participates in the oxidation of univalent copper.

Since this scheme presupposes dissociation, it was of interest to investigate the course of the reaction in a solvent of low dielectric constant. We therefore dissolved ascorbic acid, dye, and anhydrous cupric chloride in dioxan. In the light, the dye and ascorbic acid reacted fairly slowly, and addition of copper produced a marked retardation of the reaction. Thus, in this case, the copper was not a catalyst, but a poison, for the normal reaction. In dioxan, there is a possibility of direct reaction between dye and ascorbic acid, but the mechanism proposed by Weissberger, assuming dissociation and reaction with water, clearly can not apply, and the decolorization is retarded if the ascorbic acid combines with copper ion.

In other words, the metal ion can have an accelerating or retarding effect, depending on the nature of the solvent. Retardation by the copper ion was so intense that even illumination by a 500 w lamp for two minutes failed to produce any appreciable decolorization. It is interesting that trilon also showed a reversed effect in dioxan; addition of trilon complexed the copper ion and, naturally, accelerated the reaction.

On the other hand, when we carried out the reaction in pyridine, which has a dielectric constant seven times that of dioxan, we observed a very rapid reaction. Pyridine itself is basic, and, probably for this reason, decolorization occurred rapidly even in the absence of copper.

2. Acceleration of the Peroxidation Process in the System Metal Ion – "Carrier" – Substrate

The oxidizing action of hydrogen peroxide on Indigo-Carmine, investigated in our laboratories by L. S. Kitsenko, provides an interesting example of a reaction which is considerably accelerated at the interface between benzene and water [12]. We found that addition of a divalent manganese salt to a mixture of hydrogen peroxide and dye in aqueous solution produced a further acceleration of the process. It is known that divalent manganese ions possess no catalytic function; it is highly improbable that the manganese ion can form a compound with benzene. Consequently, in the system benzene – hydrogen peroxide – dye, the manganese ion could only have a weak orienting influence, without combining with any of the compounds formed; the spectrum of the Indigo-Carmine solution showed no significant change when manganese ions were added. This case is probable an example of a very weak bond between the metal ion and the "carrier" and reaction substrate. Nevertheless, catalysis was observed.

TABLE 1

The Accelerating Action of Mn^{2+} on Catalysis by Benzene and Protein (Legumin) of the Reaction of Oxidation of Indigo-Carmine by Hydrogen Peroxide. (The interaction was of the first order with respect to the dye, $t° = 23°$, pH = 6.8)

Catalytic system	$k \times 10^{-2}$, min^{-1}	Notes
Benzene emulsion	0.5	The method of observation was spectrophotometric
The same + manganese	1.4	
Protein	3.0	
Protein + manganese	3.6	

It was found that glutamic acid and protein (legumin and casein) were more active catalysts for this reaction; protein was almost six times as active as benzene.

Addition of manganese ions to solutions of these substances increased their catalytic effects. The link between manganese ion and protein, which it activated, was undoubtedly stronger than the link between manganese and benzene. But the activating action of the manganese ion was considerably less on protein than on benzene (Table 1).

It is undoubtedly possible to find examples of activating effects by metal ions on ferments and other biocatalysts, where it is difficult to suppose the formation of individual intermediate compounds; probably, such cases should include the action of potassium on the transphosphorylase ATF-phosphopyruvate or the action of calcium on actomyosin [1].

3. Decomposition of Hydrogen Peroxide by a Catalytic System Consisting of Complex Ion – Addendum

Let us consider another case, where the ion is enveloped by close bonding with an addendum, and usually emerges from the reaction preserving the same envelope with which it entered into the process. This envelope, i.e., the addendum, can markedly change the activity and selectivity of the ion. We showed in a series of papers [13, 14] that combination with various addenda could alter the capacity of the copper ion for decomposing hydrogen peroxide within very wide limits. Copper ion complexes with biuret, amines, and diamines were almost a million times as active as the simple ion.* For this to be so, it is essential that the coordination sphere of the copper ion should contain nitrogen atoms forming a complex of the chelate type, i.e., a complex containing a "pincer" grouping. The coordination number of the copper should be four, and the complex as a whole should not be stable. It is interesting that some American authors reached the same conclusions considerably later [15] when investigating another reaction, namely the hydrolysis of certain organic compounds, also accelerated by copper complexes.

Thus, the above characteristics – labile nature, coordinated nitrogen, and pincer-type structure – are important features controlling the general catalytic activity of the complex.

In all the cases we have investigated, a large excess of addendum in solution reduced the activity owing to formation of compounds with a coordination number of six. Increase in pH at first led to a rise and then to a drop in activity. With increasing hydrogen peroxide concentration, the activity increased at first and then became constant. We presumed that reaction occurred as the result of formation of a labile intermediate. Addition of methyl methacrylate to the reaction mixture had no retarding effect, so that a radical-chain mechanism appeared to be highly improbable in this case.

The variety of catalytically active structures of the copper amine type raises the very important question as to why there are no natural ferments which decompose hydrogen peroxide, but contain copper instead of iron. Measurements showed that the activation energy for the decomposition of hydrogen peroxide, catalyzed by copper complexes, was the same as that for the uncatalyzed reaction. Consequently, acceleration was achieved as the result of an entropy factor.

However, when investigating oxidation reactions which were accelerated by copper complexes, we found that the same catalysts, which accelerated hydrogen peroxide decomposition without altering the activation energy, did lower the activation energy for oxidation of pyrogallol [10].

4. Oxidation of Polyphenols. System Complex Metal Ion – Protein

The oxidation of pyrogallol was investigated by Korpusova and the author, with the object of finding complex compounds which would serve as models for the ferment polyphenoloxidase [10]. We found that the copper complexes with monoethanolamine and with ethylenediamine showed high catalytic activity for this reaction. An interesting fact was noted in passing: The amines, used as addenda, were themselves weak catalysts for this reaction. Their activity was increased by complex formation. This increase depended on the nature of the amine: it was slight with ethylenediamine, although the amine itself showed relatively high activity, and the reverse was true for ethanolamine. The different cases of activation, as the result of combination of the copper ion with an amine, are shown in Fig. 4.

Figure 4 shows the activity of the copper ion taken as unity; the addendum (in this case monoethanolamine) by itself showed weak activity. Combination with protein increased the activity of the amine; there was a greater increase as the result of complex formation, and the activity was still further increased by fixation of the complex on protein (albumin).

*According to our results, the complex formed by the copper ion with the polymer – polyethylenepolyamine at pH 9.4 – shows almost the same activity as the ethylenediamine complex.

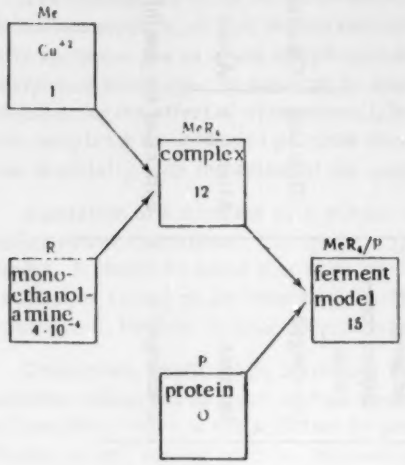

Fig. 4. Diagram showing the sequence for construction of a model for the ferment polyphenoloxidase.

If we compare the experimental results for the decomposition of hydrogen peroxide with those for the oxidation of pyrogallol, then it is easy to see that, in the first case, we are dealing with a model which has no chance of competing with the iron complexes, which are stable and capable of activation by adsorption. However, in the second case, our model contains the same metal as the natural ferment and has considerable resemblances to a biocatalyst. Our model of the active group of polyphenoloxidase shows a capacity for adsorption activation by fixation on proteins.

By fixing copper complexes with monoethanolamine on proteins (albumin, casein, and legumin), we obtained complex catalysts which were active as the result of a reduction in the activation energy. With these catalysts, the activation energy for pyrogallol oxidation was reduced to 5000 kcal/mole (the value of the uncatalyzed reaction was 18,000 kcal/mole), and the activity was almost 15 times that of the polyphenoloxidase produced by the method of Mikhlin and Szent-Györgyi [16].

Thus, catalysts of this type showed high activity, and acted by reducing the activation energy. They can therefore be considered as ferment models.

5. Discussion of Results

Table 2 shows the actions of the metal ions considered above. One of the most widespread and least specific effects is the ability of variable valency ions (iron, copper, cobalt, etc.) to give rise to chain processes. It is a very complicated problem to say how widespread in biological systems are catalytic effects associated with chain reactions, i.e., with the action of free radicals. It is clear that the action of a number of ferments, catalases in particular, is associated with the formation of intermediate products and not with development of chains. However, as Mikhlin says [16], the question of a chain mechanism for the action of lipoxidase remains unsolved at present.

There are ion-substrate catalytic systems which catalyze redox processes and produce polarization effects (Table 2, columns 3 and 4).

Reduction of a metal ion (e.g., copper) by a hydrogen donor, and subsequent oxidation of this ion by a hydrogen acceptor with water participating, may partially explain the effects of metal ions on the activity of dehydrogenases.

As far as can be judged from the existing data, this type of catalytic system accelerates the reaction by lowering its activation energy.

In more complex systems including a "carrier," some examples of which are given in Table 2, columns 5-7, the metal ion plays the role of an "orientator," drawing together the substrate and catalyst.

The problem of the change in ion charge remains unsolved; in certain cases (for instance, in the oxidation of the dye described in this paper), there is every reason to believe that the ion charge does not alter. In this case, acceleration of the reaction is associated with an increase in the activation entropy, while the activation energy remains unchanged.

Complex formation with the participation of specific addenda, is undoubtedly an important means of activating a metal ion. This not only produces an enormous increase in activity, but can give rise to a qualitative change in the nature of the ionic action.

We have already noted that a model of the active group of the ferment catalase, consisting of copper amine complexes, can be nearly a million times as active as the simple ion; the zinc complex, which is a component of the ferment carboanhydrase, shows properties completely lacking in the simple ion. The same may be said of the action of the manganese ion in chlorophyll.

TABLE 2

Different Cases of Catalytic Action by Systems Containing Metal Ions

	Chain initiation	Formation of metal ion – – substrate complex		Formation of metal ion – carrier – substrate complex			Formation of complex with addendum; coordination number 4	Activation of complex by fixation on carrier	
		redox process	polarizing action	carrier inert; weak bonding with ion	carrier active; weak bonding with ion	carrier active; strong bonding with ion		carrier nonspecific	carrier specific
1	2	3	4	5	6	7	8	9	10
Reaction	Benzaldehyde oxidation under influence of cobalt ion	Ascorbic acid oxidation under influence of copper ion	Keto acid decarboxylation under influence of aluminum ion	Catalysis by Mn ion in benzene emulsion for the oxidation of Indigo-Carmine by hydrogen peroxide	The effect of glutamic acid in increasing the catalytic activity of the manganese ion for the same reaction	Activation of aminopolypeptidase by magnesium or manganese ions; activation of flavoproteins by copper ions	Hydrogen peroxide decomposition under the influence of amine copper complexes or hemin; pyrogallol oxidation under the influence of copper complexes	Pyrogallol oxidation under the influence of copper complexes fixed on proteins	The action of catalase ferments
Activation energy	Decrease	Decrease		Unchanged	Unchanged	Decrease	Unchanged	Decrease	Decrease
Activation entropy				Increase	Increase		Increase	Alters	Alters
Ionic charge	Alters	Alters	Unchanged	Unchanged	Unchanged	Unchanged	Unchanged	Both cases are possible	

The mechanism of the action of model complexes is partly associated with the formation of very labile intermediate products, so that the acceleration is normally "entropic" in character. This "entropic" character clearly applies to the catalysis of hydrogen peroxide decomposition. However, the effect has a mixed character in polyphenol oxidation. In catalysis by complexes, the metal ion charge can alter (it is sufficient to recall the mechanism for the effect of cytochromes), but it can also remain unchanged. The catalytic action of copper amine complexes on hydrogen peroxide decomposition is evidently not associated with a valency change, and differs essentially from the action of the simple ion.

Activation of a complex with protein carriers gives rise to ferment models which merit this designation to a greater extent than others. The system copper-monoethanolamine on casein (or albumin) belongs to this class of model. It should be noted that these systems, which are shown in column 9 of Table 2, considerably reduce the activation energy of the catalyzed reaction. They resemble ferments, not only in structural type and kinetic characteristics, but also in their thermodynamic features.

Complexes, which act by increasing the entropy factor, are not activated by adsorption on carriers. This observation refers, not so much to the complex itself, as to the association of complex and reaction. Thus, a given complex, which is not activated by proteins for hydrogen peroxide decomposition and does not reduce the activation energy for this reaction, behaves quite differently for the oxidation of polyphenols.

The most efficient catalysts – ferments – are shown in column 10 of Table 2. Their active groups are frequently porphyrin complexes. It is precisely these compounds which satisfy the complex requirements characteristic of biological systems. The porphyrin complexes are active, sufficiently stable, and have a planar structure, the coordination number of their metal ion is four, the ion is surrounded by nitrogen atoms, and, finally, these complexes can be activated by adsorption on proteins.

The reduction in activation energy, in catalysis by complexes adsorbed on proteins, shows the energetic nature of the carrier effect. In the case of polyphenol oxidation described above, the bond between complex ion and protein is through the amino groups, since the catalyst is inactivated by treatment of the protein with formaldehyde. By means of this bond, the complex ion reacts energetically with the complex aggregate of polypeptide chains in the protein. In 1941, Szent-Györgyi [17] compared proteins with metals, and suggested that migration of energy into the protein was based on an electronic mechanism. In 1948, I expressed the view that the phenomenon of adsorption activation was generally based on the action of "conducting paths," consisting of aggregates of carrier atoms, to which energy could be transferred irrespective of the transfer mechanism [18]. Commer, Townsend, and Pake [19] showed that free electrons could be detected in dry animal and vegetable tissue by means of electron paramagnetic resonance, and Blyumenfel'd and Kalmanson [20] showed that these were the delocalized electrons of the actual proteins.

It appears certain that those complex compounds which are capable of entering into energetic interaction with the electron systems of proteins acquire an additional capacity to reduce the activation energy of the catalyzed reaction, and thus have an advantage over complexes which do not show these properties. In particular, with reference to hydrogen peroxide decomposition, the iron – porphyrin complexes are in a better position than the copper – amine complexes, and therefore, as the result of evolution and selection, highly active catalysts of the catalase type have developed on the basis of iron compounds instead of copper.

Although in the course of biochemical evolution only a few complexes have developed and become "perfected" to the level of a specialized ferment structure, yet other mechanisms for ionic action, described above, are evidently precursors of ferment mechanisms and play an important role in catalytic metabolic processes.

Numerous kinetic effects, which are usually associated with transformations of organic substances in cells, are actually due to catalysis by very small amounts of metal ions. Their remarkable capacity to produce catalytic action, as the result of weak orientation and polarization effects, may provide a basis to explain the puzzling role of many "microelements."

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*Original Russian pagination. See C.B. Translation.

KINETIC METHOD FOR DETERMINATION OF ADSORPTION COEFFICIENTS

1. ADSORPTION COEFFICIENTS OF WATER, ETHER AND ETHYLENE ON ALUMINA

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The kinetics of the degradation reaction of ethyl alcohol on alumina have been studied at two temperatures: 250° and 430° The effect which additions of water, ether, ethylene, and argon have on the process rate has been investigated. The adsorption coefficients of water, ether and ethylene were calculated from the experimental data.

It is impossible to develop a theory for a series of catalysts without a thorough and detailed study of catalytic processes and their kinetics. A kinetic investigation of a reaction gives the most accurate evaluation of the activity of the catalyst – according to the rate constant.

Existing methods for investigating the kinetics of heterogeneous catalytic processes as a rule enable only an apparent rate constant to be determined, and not the true one. The apparent rate constant, found experimentally, does not characterize the catalytic activity of the sample very clearly, especially in those cases where a diffusion process is superimposed on the fundamental chemical process.

However, in the absence of diffusion inhibition, when the reaction takes place in the kinetic zone and the apparent rate constant is proportional to the true constant, a whole series of parameters, which characterize the adsorption stage of the process, must be known in order to calculate the value of the latter. The adsorption coefficients are such parameters.

Since it is usually impossible to investigate the kinetics of the course of a catalytic reaction actually on the catalyst surface, the processes which occur there must be studied indirectly from the change in composition of the gas phase during the reaction. As the adsorption isotherm* is a function of the surface and bulk concentrations of the substances, it always appears in kinetic equations for heterogeneous catalytic reactions. This introduction of the adsorption isotherm into the kinetic equation means that the apparent rate constant contains the adsorption coefficients of all the gaseous components as well as the true rate constant. Hence, calculated values for these adsorption coefficients are clearly very necessary for the calculation of the true rate constant.

A knowledge of the adsorption coefficients by themselves is also very important in investigating the interaction of substances (which participate in the reaction) with activated catalyst centers, and also in explaining the mechanism of the elementary catalytic step.

There are two possible methods for finding adsorption coefficients – adsorption and kinetic. However the direct adsorption method, i.e., finding the adsorption equilibrium constant from the adsorption isotherm, is of no

*On condition that the adsorption equilibrium between the surface and bulk phases is attained very quickly, and is practically unaffected by the course of the chemical reaction.

use in a given case, since the adsorption and catalytic regions of the surface are different for most catalysts, particularly with regard to adsorption properties. As a result, these different regions of the surface can have different adsorption coefficients [1]. Since the adsorption method gives an average value of the adsorption coefficient for the whole surface, the results cannot be used to calculate the true rate constant.

The standard method is the kinetic one, which makes it possible to determine adsorption coefficients which are characteristic of the adsorption properties, i.e., the catalytically active sections of the surface.

The fundamental principals of the kinetic method were developed over twenty years in the work of Langmuir and Shvab, and its first application was to static systems. Attempts to apply it to flow systems were unsuccessful until 1942, when the basic differential kinetic equation for reactions in a flow system was worked out [2]. At this time there was much work being done on the development of a kinetic method suitable for flow systems (cf. Soviet workers Balandin, Frost, Panchekov, and others). Now it is used in research as a basic method for studying heterogeneous catalytic processes.

The kinetic method is based on a study of the relation between the reaction rate and the different factors which determine the experimental conditions – temperature, pressure, volume rate, and composition of mixture present in the reaction zone.

If the rate of a heterogeneous catalytic reaction is to be determined in terms of the number of moles of original material converted in unit time on unit surface, the differential kinetic equation for the reaction in a flow system will be (see Frost [3]):

$$w = v_0 \frac{dy}{S_0 dl}, \tag{1}$$

where w is the reaction rate; v_0 is the volume rate of introducing the initial material to the reactor in ml, g, moles, etc., in unit volume, for unit weight of catalyst and unit time; y is the degree of conversion of the original material; S_0 is the catalytically active surface in unit length of a layer of catalyst, in the direction of motion of the stream of material and l is the distance from the beginning of the reaction zone to the point at which the degree of conversion y is attained.

Some general conclusions from hydrodynamic considerations of this equation have been given by Panchenkov [4].

For the monomolecular irreversible reaction

$$A_1 \longrightarrow \nu_2 A_2 + \nu_3 A_3 + \ldots + \nu_k A_k$$

the expression for the reaction rate has the form [5]:

$$w = k n_0 \frac{b_1 p_1}{1 + \sum_1^k b_i p_i}, \tag{2}$$

where n_0 is the number of moles of material adsorbed at complete coverage by unit surface; k is the true reaction rate constant (unit time^{-1}); b_1 and p_1 are the adsorption coefficient and partial pressure of the original material, and b_i and p_i are similar values for the i-th component.

To integrate Eq. (1) the expression for the reaction rate (2) must be substituted in it, in which the partial pressures are represented as functions of the degree of conversion. The final integrated equation, can be written down in several ways (Balandin's equation, Frost's equation, Panchenkov's equation), but if the symbols are unified, they can all be reduced to one form [5]:

$$v_0 \ln \frac{1}{1-y} = \frac{k n_0 S b_1 P}{1 + n + \sum_2^k [(1 + b_i P)\delta_i + b_i \nu_i P]} + \frac{n - b_1 + \sum_2^k b_i P}{1 + n + \sum_2^k [(1 + b_i P)\delta_i + b_i \nu_i P]} \cdot v_0 y, \tag{3}$$

where P is the total pressure of the system; S = SL, where L is the length of layers of catalyst; ν_i is the stoichiometric coefficient of the i-th component; $n=\sum_2^k \nu_i - 1$ is the change in the total number of moles due to reaction; δ_i is the dilution, i.e., the relation of the number of moles of the i-th component to the number of moles of reacting material in the original mixture.

Equation (3) is the most general; no assumptions were made in its deduction apart from those which lie at the basis of the kinetic method.

Equation (3) contains three independent variables v_0, P, and δ_i, which can have arbitrary values, and the variable y which depends on them, and which is experimentally determined. In addition, the equation has (K + 1) parameters (K adsorption coefficients and the product of the constant values kn_0S). To find these parameters for the general case, (K + 1) equations for the system obtained by varying v_0, P and δ_i must be solved. But it should be noted that in Eq. (3) in its general form, variation of only v_0 or P or δ_i, or v_0 and P, or v_0 and δ_i, simultaneously, does not enable all (K + 1) parameters to be determined. On the other hand, this equation can be modified in relation to the characteristics of a kinetic catalytic reaction, and this results in a different method of determining the parameters.

Some methods of determining kinetic parameters, which utilize the basic Eq. (3) in one form or another, are examined below.

Equation (3) is used in its most general form in Frost's kinetic method [6].

If we denote

$$\alpha = \frac{kn_0Sb_1P}{1+n+\sum_2^k [(1+b_iP)\delta_i + b_i\nu_iP]}, \tag{3a}$$

$$\beta = \frac{n - b_1P + \sum_2^k b_i\nu_iP}{1+n+\sum_2^k [(1+b_iP)\delta_i + b_i\nu_iP]}, \tag{3b}$$

Equation (3) has the form

$$v_0 \ln \frac{1}{1-y} = \alpha + \beta v_0 y \tag{4}$$

Equation (3) was first obtained in this form by Frost [3]. It has been repeatedly applied to describe the kinetics of conversion of different substances on solid contacts.

The values of α and β are functions of the parameters of Eq. (3) and are constant at constant temperature, pressure, and composition of the original mixture. The dependence of the degree of conversion y on the rate of introduction v_0 has been examined experimentally. Equation (4) when plotted in the coordinates $v_0 \ln \frac{1}{1-y}$, $v_0 y$ gives a straight line, from which α and β can be determined from the ordinate intercept and the gradient, respectively. The value of α during a flow reaction in the kinetic range is proportional to the true rate constant, and can therefore be studied as an apparent rate constant. The value of β depends on the corresponding adsorption coefficients. Theoretically $-\infty < \beta < 1$.

If experiments are carried out with a pure initial material to study the dependence of α and β on pressure, the equation:

$$\frac{1-\beta}{\alpha} = \frac{1}{kn_0S} + \frac{1}{kn_0Sb_1}\cdot\frac{1}{P}, \tag{5}$$

which gives a straight line when plotted in the coordinates $\frac{1-\beta}{\alpha}$, $\frac{1}{P}$ enables kn_0S and b_1 to be calculated.

If the pressure in the system is constant, and the initial material is diluted with an inert material which is not adsorbed on active centers of the catalyst (i.e., its adsorption coefficient is zero), the values of kn_0S and b_1 can be found in a similar way from the equation:

$$\frac{1+\beta}{\alpha} = \frac{1}{kn_0S} + \frac{1}{kn_0Sb_1P} \cdot (1+\delta_i) \tag{6}$$

by studying the dependence of α and β on the dilution δ_i.

It can be shown that the values of $\alpha/S(1-\beta)$ is the rate with which the reaction proceeds at the very initial layer of the catalyst. Consequently since

$$w = \frac{v_0}{S_0} \frac{dy}{dl}, \tag{7}$$

the initial rate is

$$w_0 = \frac{v_0}{S_0} \left| \frac{dy}{dl} \right|_{l \to 0}. \tag{8}$$

From Eq. (4) we find

$$\left| \frac{dy}{dl} \right|_{l \to 0} = \frac{S_0}{v_0 S} \cdot \frac{\alpha}{1-\beta}. \tag{9}$$

Substituting (9) in (8) we obtain

$$w_0 = \frac{\alpha}{S(1-\beta)} = kn_0 \frac{b_1P}{1+b_1P}. \tag{10}$$

Thus, the initial reaction rate, which it is usually impossible to obtain by direct experimental measurements, can be obtained by Frost's kinetic method from results obtained at high degrees of conversion.

To determine the adsorption coefficients of reaction products or foreign materials, the effect of adding these materials to the original must be studied at a constant value of α. When the initial material enters the reaction zone in a mixture with one of the reaction products or foreign materials, the value $1/\alpha$ can be represented as a linear function of the conversion:

$$\frac{1}{\alpha} = \frac{1}{\alpha_0} + D_i\delta_i, \tag{11}$$

where

$$\frac{1}{\alpha_0} = \frac{1+n+\sum_2^k b_iP}{kn_0Sb_1P} \text{ and } D_i = \frac{1+b_iP}{kn_0Sb_1P}. \tag{12}$$

Equation (11), when plotted in the coordinates $1/\alpha$, δ_i gives a straight line, whose gradient is equal to D_i. As a result of experiments with inert diluents, which are not adsorbed on active centers of the catalyst, the relation is found:

$$D_0 = \frac{1}{kn_0Sb_1P}. \tag{13}$$

From the values obtained for D_i and D_0:

$$b_i = \frac{1}{P}\cdot\frac{D_i}{D_0} - \frac{D_0}{D_0} \tag{14}$$

– the adsorption coefficient of the material added.

Thus, by applying Frost's kinetic method all the parameters of the kinetic Eq. (3) can be determined. However, it is only found to be practical for determining the adsorption coefficients of the reaction products (1). The adsorption coefficient of the initial material cannot be determined by this method because, in all the cases studied, the value of β has a constant value, within experimental error, equal to unity, over a wide range of conversion. This makes it impossible to use Eqs. (5) and (6) given above to determine the adsorption coefficient of the initial material.

Frost's kinetic method is only usually applied in cases where the degree of conversion depends on the pressure. If a change in pressure does not substantially affect the degree of conversion,* it becomes impossible to determine the adsorption coefficient. As a result, when $y \neq f(P)$, the term which does not contain P can be neglected in the denominator of the expression for α (3a) and in both numerator and denominator of the expression for β (3b). Then Eq. (3) has the form:

$$v_0 \ln\frac{1}{1-y} = \frac{kn_0S}{\sum_2^k(\delta_i + \nu_i)z_i} + \frac{\sum_2^k \nu_i z_i - 1}{\sum_2^k(\delta_i + \nu_i)z_i}\cdot v_0 y, \tag{15}$$

where $z_i = b_i/b_1$ – the relative adsorption coefficient.

It can be seen from Eq. (15) that in this case, any method of varying v_0 and δ_i only allows the relative adsorption coefficients to be determined.

A method for determining relative adsorption coefficients was developed thoroughly by Balandin and coworkers. A detailed review of it has been given [10], so we will only outline the basic ideas here.

The determination of these coefficients is based principally on a study of the inhibiting effect of reaction products or foreign materials added to the original.

If the composition of the initial material is changed it is possible, generally speaking, to obtain a system of the K-equation type (15) in which δ_i is the variable. The general methods of solving such a system of equations have been given [10]. The solutions are calculated formulae for calculating the relative adsorption coefficients and the value of kn_0S. The solution can be simplified by introducing a series of additional conditions (for example, the case of binary mixtures of the initial material with each of its reaction products or with foreign materials, and the case of equal percentage binary mixtures and so on). The advantage of this method, based on an application of Eq. (15), is that it can be used at any degree of conversion.

In this way, the independence of the degree of conversion on pressure superimposes the limitation on the use of the kinetic method for determining adsorption coefficients. In other words, the nondependence of $\underline{y}$ on P makes it impossible to find their absolute values, which is very essential in some cases.

In deducing Eqs. (3-15), it was assumed that the reaction rate in the original Eq. (1), $\underline{w}$, varied along the catalyst layer. This, however, does not always take place. In fact, in at least two cases, $\underline{w}$ is constant along

*See for example [7, 8, 9].

the layer. In the first place, when adsorption of the initial material is very high and of the products low, so that $b_1 P_i \gg \sum_2^k b_i P$ and 1, then

$$w = kn_0, \tag{2a}$$

i.e., the reaction is of zero order. Substituting (2a) in (1) and integrating we obtain

$$v_0 y = kn_0 S = \text{const}, \tag{16}$$

In this case the number of moles of original material converted in the reactor in unit time is independent of the rate of introduction; also y is linearly dependent on $1/v_0$. The value of $v_0 y$ determined experimentally gives the value of $kn_0 S$ directly.

Secondly, w is constant when the partial pressure of the original material is constant along the catalyst layer. This is practically realized at very low degrees of conversion.

When the degree of conversion is low, the change in partial pressures of the components can be neglected. Then, in Eq. (2), $p_1 = p_{01}$; $p_2 = p_{02}$; $p_i = p_{0i}$, where p_{0i} is the pressure of the i-th component in the original mixture, and:

$$w = kn_0 \frac{b_1 p_{01}}{1 + \sum_1^k b_{0i} P_i} = kn_0 \frac{b_1 p_{01}}{1 + p_{01} \sum_1^k b_i \beta_i} \tag{2b}$$

Substitution of (2b) in (1) and integration gives:

$$v_0 y = kn_0 S \frac{b_1 p_{01}}{1 + p_{01} \sum_1^k b_i \beta_i}. \tag{17}$$

In this case $v_0 y$ is also constant and does not depend on v_0. If the initial material alone is introduced to the reactor, $p_{01} = P$; $p_{02} = \ldots = p_{0i} = 0$ and Eq. (17) becomes:

$$v_0 y = kn_0 S \frac{b_1 P}{1 + b_1 P}. \tag{18}$$

Equation (18) tallies with Eq. (5) and can be obtained from the general Eq. (3) if, at small degrees of conversion, it is assumed that:

$$\ln \frac{1}{1 - y} \simeq y. \tag{19}$$

Substituting (19) in (3) we obtain

$$v_0 y = \frac{\alpha}{1 - \beta}.$$

Since the value of $\alpha/S(1 - \beta)$ equals the initial reaction rate w_0 (see above):

$$\frac{v_0 y}{S} = w_0 = kn_0 \frac{b_1 P}{1 + b_1 P}. \tag{18a}$$

Hence, splitting up the logarithm of Eq. (19), which is often done to simplify the general Eq. (3), has the same physical significance as the assumption that the partial pressure is constant along the layer of the catalyst at low degrees of conversion.

If the dependence of $v_0 y$ on the pressure P is studied, $kn_0 S$ and b_1 can be found from Eq. (18). If a reaction product or foreign material is added to the initial material and the dependence of $v_0 y$ on the dilution δ_i is studied, it is possible to determine the adsorption coefficient of the added material from Eq. (17).

In this case, if the reaction rate is independent of the pressure P, Eq. (17) becomes:

$$v_{0y} = \frac{kn_0 S}{k + \sum_i z_i \delta_i} \quad . \tag{17a}$$

When the pure initial material is introduced to the reactor, measurement of $v_0 y$ gives $kn_0 S$ directly. Relative adsorption coefficients are determined from:

$$\frac{1}{v_{0y}} = \frac{1}{kn_0 S} + \frac{z_i}{kn_0 S} \cdot \delta_i . \tag{20}$$

The method described, based on the application of low degrees of conversion, was put forward by Balandin [11], and later developed in the work of Prater and Lago [12, 13].

It should be noted that studying reaction kinetics at low degrees of conversion is accompanied by a whole series of experimental difficulties, because in the usual method the accuracy of the results decreases sharply with decreasing degree of conversion. At the same time, Eq. (17)-(20), used to calculate some of the parameters, are more accurate, the lower the degree of conversion. So, as a rule, a kinetic study of catalytic reactions for determining adsorption coefficients and rate constants is carried out at degrees of conversion not lower than 5-10%, i.e., when Eq. (17)-(20) are only approximate, or at high degrees of conversion when the integral kinetic equation can be applied.

Only recently, a series of American workers [12-14] developed a differential reactor, which can be used for degrees of conversion <1%. The use of such low degrees of conversion ensured great accuracy of the kinetic Eq. (17)-(20), which these workers used, and made it possible to study practically any reaction – irreversible or reversible. This is a great advantage of the differential reactor, since the usual (integral) reactors can only be used in cases where there is a sufficiently high equilibrium degree of conversion. Apart from this, work at high degrees of conversion is very often complicated by secondary processes, which make kinetic studies difficult. These processes are absent at low degrees of conversion.

In spite of the advantages of the differential reactor, it cannot take the place completely of the integral one, and a detailed kinetic study of a reaction must include both of these experimental methods.

In concluding this survey of the kinetic method, we must point out that the main possibility of calculating all the parameters for the kinetic mechanism of some catalytic process usually depends on improving existing methods or developing new methods of investigation.

The aim of this present work was to determine adsorption coefficients for components of reactions whose kinetics and mechanisms had been studied adequately, and to try to give more detailed kinetic schemes of these reactions from the results obtained.

One such reaction studied was the dehydration of ethyl alcohol on alumina, which, from the ample literature references, proceeds in a comparatively simple way, without any secondary processes.

The effect of dilution of the initial ethyl alcohol with reaction products (water, ether, ethylene) and an inert diluent (argon) on the dehydration reaction rate was studied. The experimental results were treated by Frost's kinetic method.

All experiments were carried out at atmospheric pressure in the usual flow-type apparatus with automatic feeding of the initial material. The rate of feeding varied from 0.46 to 6.07 mmole $\cdot g^{-1} \cdot min^{-1}$. The catalyst was manufactured stick alumina; weight of dry, granular material ~0.5 g/cc; average dimensions of granules ~3 mm. Alcohol-water mixtures were prepared from redistilled alcohol, and were accurately weighed on an analytical balance; ether-alcohol mixtures were prepared in an analogous way from absolute alcohol and ether. The gases (argon and ethylene) were carefully dried before admission to the apparatus by passing them through a trap, which was cooled with dry ice and alcohol to −35°, and a column of Al_2O_3 and P_2O_5 which had been baked. Ethylene given off during the reaction was collected over a saturated NaCl solution; analysis of the liquid product of catalysis was analyzed by a method given in [15]. The degree of conversion was determined to ± 2%.

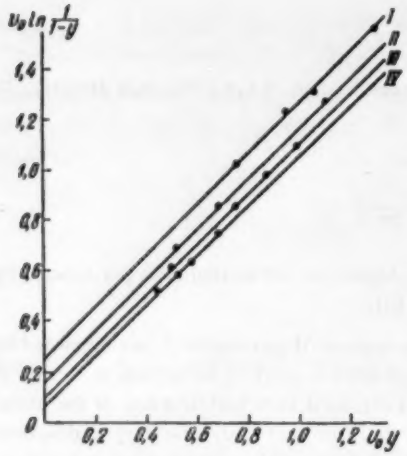

Fig. 1. Temperature 250°. Dilution by water: 1) δ = 0; 2) δ = 0.28; 3) δ = 0.64; 4) δ = 1.03.

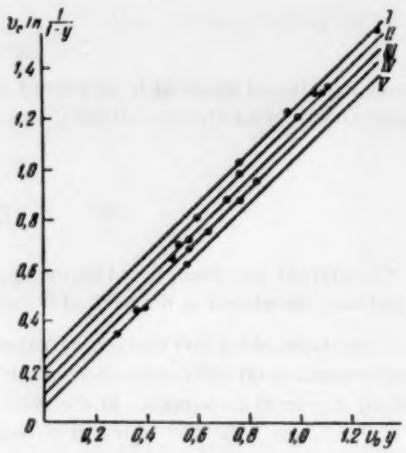

Fig. 2. Temperature 250°. Dilution by ether: 1) δ = 0; 2) δ = 0.23; 3) δ = 0.50; 4) δ = 0.72; 5) δ = 1.48.

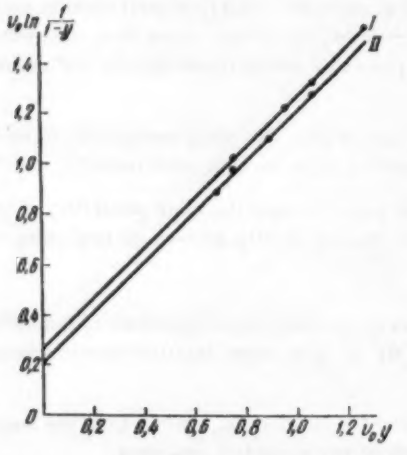

Fig. 3. Temperature 250°. Dilution by argon; kinetics for the two extreme cases: 1) δ = 0; 2) δ = 4.23.

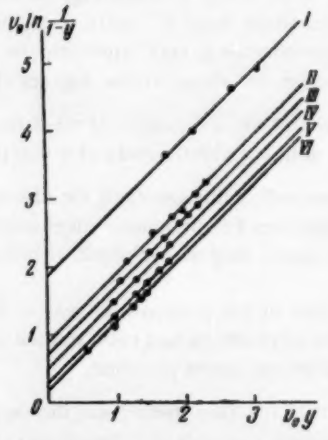

Fig. 4. Temperature 430°. Dilution by water: 1) δ = 0; 2) δ = 0.93; 3) δ = = 1.34; 4) δ = 1.83; 5) δ = 2.80; 6) δ = 4.04.

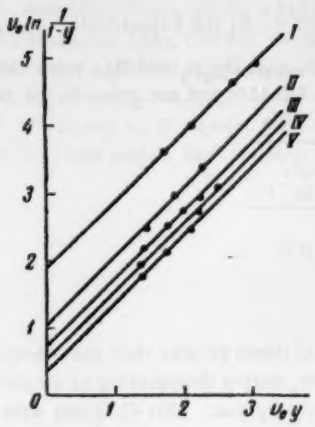

Fig. 5. Temperature 430°. Dilution by ethylene: 1) $\delta = 0$; 2) $\delta = 1.20$; 3) $\delta = 2.28$; 4) $\delta = 3.35$; 5) $\delta = 4.10$.

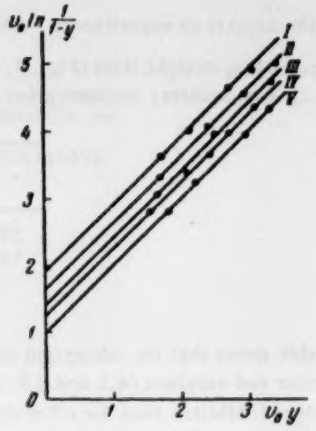

Fig. 6. Temperature 430°. Dilution by argon: 1) $\delta = 0$; 2) $\delta = 0.52$; 3) $\delta = 1.00$; 4) $\delta = 1.41$; 5) $\delta = 2.10$.

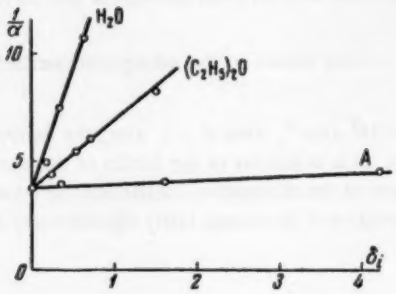

Fig. 7. Temperature 250°. Relation between $1/\alpha$ and δ_1.

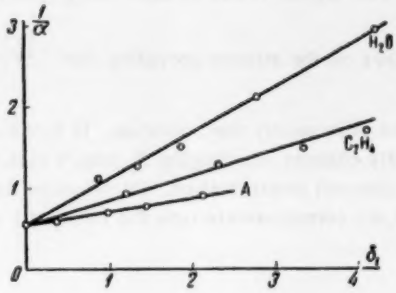

Fig. 8. Temperature 430°. Relation between $1/\alpha$ and δ_1.

Experiments were carried out at two temperatures: 250 and 430°. At 250° ethyl alcohol decomposes to ether and water only, and at 430° to ethylene and water:

$$C_2H_5OH \xrightarrow{250^\circ} (C_2H_5)_2O + H_2O$$
$$C_2H_5OH \xrightarrow{430^\circ} C_2H_4 + H_2O$$

Three series of experiments were carried out at each temperature: dilution by water, ether and argon (250°), and by water, ethylene and argon (430°). Figures 1-8 contain the experimental results. Figures 1-6 show that the experimental results fit in well with Frost's equation; the value of β is the same in all cases and equals unity within experimental error. The values of the constant α was found algebraically in all cases from the formula

$$\alpha = \frac{\sum_1^N \left(v_{oj} \ln \frac{1}{1-y_j} - v_{oj} y_j \right)}{N}.$$

where N is the number of experiments. When plotted in the coordinates $\frac{1}{\alpha}$, δ_1 the experimental points lie nicely on the corresponding straight lines (Figs. 7, 8). The values of D_{H_2O}, D_{ether}, $D_{C_2H_4}$ and D_A were calculated by the method of least squares; the adsorption coefficients were found by Eq. (14) and are given in the table;

t,°C	b_{H_2O}, atm^{-1}	b_{ether} atm^{-1}	$b_{C_2H_4}$, atm^{-1}
250	$0{,}9 \cdot 10^2$	$0{,}2 \cdot 10^2$	
430	2,0	—	0,8

The table shows that the adsorption coefficient of water is several times greater than the adsorption coefficients of ether and ethylene (4.5 and 2.5, respectively). Consequently, during dehydration of alcohol, water exerts a stronger inhibition than the other reaction products – ether and ethylene. This disagrees with earlier results [1], where it was found that the adsorption coefficients of water and ethylene had very nearly the same value. The value of the adsorption coefficient obtained must have been due to insufficiently careful drying of the ethylene used as diluent.

The adsorption coefficient, as can be seen from the table, decreases sharply with increasing temperature, which is associated with the significant heat of adsorption of water on active centers of alumina (~0.1 kcal/mole).

From Fig. 7, the value of $1/\alpha$ and, consequently, of α, too, varies negligibly at 250° on dilution of the alcohol with argon. It can be seen easily from Eq. (3a) that on dilution with an inert diluent, α will have little dependence on the dilution providing that $\sum_i^k b_i p_i P \gg 1 + n + \delta_i$. Our values of the adsorption coefficients for water and ether satisfy this condition. In fact since their sum is $\sim 10^2$ atm^{-1}, when P = 1 atm, the denominator of (3a) hardly changes on changing δ from 0 to 4, so that the change in α is almost in the limits of the accuracy of its experimental determination. On the other hand, at 430° the sum of the adsorption coefficients of water and ethylene are commensurate with the value of $1 + n + \delta_i$, so the constant α decreases fairly significantly during dilution.

SUMMARY

1. The basic kinetic methods for determining adsorption coefficients have been examined.

2. It has been shown that the kinetic method enables all the basic parameters for the kinetic scheme of a catalytic process to be determined.

3. The calculated adsorption coefficients for water, ether and ethylene on alumina have been found.

4. Water has been shown to exert stronger inhibition in the dehydration of ethyl alcohol than the other reaction products.

5. The heat of adsorption of water on active centers of alumina has been evaluated.

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THE DEVELOPMENT OF CHEMICAL ACTIVITY OF INTERMEDIATE FORMS OF A TYPE OF SURFACE HYDROCARBON RADICALS IN THE HETEROGENEOUS CATALYSIS OF CARBON MONOXIDE AND OLEFINS*

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The results of the investigation of catalytic reactions of the hydrocondensation of carbon monoxide with olefins, and the hydrogenation-polymerization of olefins under the influence of small quantities of carbon monoxide in the presence of hydrogen are given, and it is shown that these support the existence of chemical activity of unstable intermediate forms on the catalyst surface. The part played by chain destruction, together with chain development, in these processes, is indicated.

It was established previously that free atoms and radicals play a part in the course of radical and radical-chain reactions under conditions of homogeneous catalysis, and the fact has been the subject of extensive investigation. For processes which take place entirely, throughout all their stages, on the surface of a solid catalyst, the significance of intermediate active forms is as yet far from being elucidated, although this problem has also been considered, primarily from the theoretical point of view [1]. The paucity of experimental facts in this field is to be explained, it would seem, by the inadequate attention which has been paid to these heterogeneously catalyzed reactions for which the part played by intermediate surface forms is most characteristic, together with the absence of generally applicable methods of investigation.

The object of this communication is the consideration of certain results which have been obtained during the investigation of heterogeneous catalytic reactions in which carbon monoxide, hydrogen, and olefins participate. The data presented are primarily of a chemical character, and should be considered as evidence of the development of intermediate active forms on the catalyst surface, and of their influence on the course and direction of the chemical process. These forms arise during the partial reduction of the carbon monoxide, or the incomplete hydrogenation of the olefins, in the presence of a catalyst consisting of a precipitated cobalt compound at 190°-200° and atmospheric pressure. It would seem from their nature that they consist of methylene-, alkyl-, or other hydrocarbon radicals.

The partial reduction of carbon monoxide by hydrogen may be expressed by the reactions [2]:

$$CO \xrightarrow{H_2} \cdot > C\!<\!\begin{matrix} H \\ OH \end{matrix} \xrightarrow{H_2} \cdot CH_2 + H_2O \qquad (1)$$

The formation of the methylene radicals has been postulated on the basis of the mechanism for the synthesis of ethylene from carbon monoxide and hydrogen proposed by Orlov [3], and applied to the higher hydrocarbons by Fischer and Tropsch [4], who first developed these processes. The specific role of the oxymethylene

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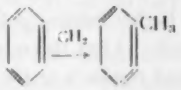
radical was observed by us [5] in the mechanism of isosynthesis during the development of side chains in branched hydrocarbons according to a condensation-dehydration scheme:

$$\equiv C-[H+HO]-CH< \longrightarrow \equiv C-CH< + H_2O \qquad (2)$$

Storch [6], and Emmett, et al. [7], assume that in the Fischer-Tropsch synthesis, the formation of all the hydrocarbon chains takes place according to this mechanism.

Experimental confirmation of the intermediate formation of methylene radicals in the synthesis of hydrocarbons from carbon monoxide and hydrogen is found in the partial conversion of benzene into toluene, observed by Zelinskii and the author, when the former is introduced into the reaction zone, the methylation of the benzene occurring at the expense of the carbon of the carbon monoxide [8]:



(3)

Similar methylation reactions have subsequently been the subject of a wide development, since it has been shown that olefins have a considerable tendency to be methylated by the products of the incomplete hydrogenation of carbon monoxide, and also to take part in other reactions in which the chemical activity of intermediate forms is found, these forms arising at the surface of a cobalt catalyst. Moreover, it can be expected that in the future there will be considerable prominence given to chemical transformations which take place in ternary mixtures of hydrogen, carbon monoxide, and an olefin, at temperatures of 190-200° and atmospheric pressure. If we leave out of consideration such incidental reactions as the hydrogenation of olefins to give paraffins containing the same number of carbon atoms per molecule, or the migration of the double bond within the olefin molecule, we may note the following fundamental reactions.

1. The hydrogenation-condensation of carbon monoxide with olefins. Within the narrow significance of this title lie the so-called "homologization" reactions: that is, the formation of higher homologues from lower ones within the olefin series, the new and the old molecule differing by one methylene group in their composition. However, in addition to the methylation of the initial olefin, it is also possible to carry out ethylation, propylation and, in general, alkylation by any alkyl group. In the general case, the formation of higher homologues may be represented schematically in the following way:

(4)

2. The hydrogenation-polymerization of olefins, in which both true polymers and hydrogenated polymers are obtained, as well as polymers and hydrogenated polymers whose number of carbon atoms per molecule is not a simple multiple of that in the initial olefin.

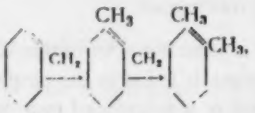
3. Destructive hydrogenation, or hydrogenation cracking, involving, in particular, the formation of non-multiple polymers and hydrogenated polymers, as well as hydrocarbons containing a smaller number of carbon atoms per molecule than the initial olefin.

The relative rates of these three types of reaction, which are often grouped together under the generic name of the "hydrocondensation" of carbon monoxide with olefins (in the broad understanding of this designation) depend on the conditions under which the reactions are carried out, especially the quantitative ratios between the components of the original mixture.

We now proceed to separate consideration of the three types of reaction.

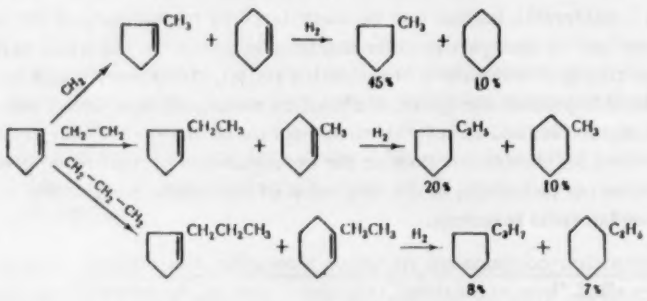
1. Hydrogenation-Condensation Reactions

The compounds whose tendency to enter into hydrogenation-condensation ("homologization") is most clearly expressed are the cycloolefins. This is due to the fact that these compounds have no tendency under these conditions to undergo hydrogenation-polymerization. The initial cycloolefin in a mixture of cyclohexene, hydrogen and carbon monoxide gives up to 10% of mono- and di-methyl derivatives [9]:



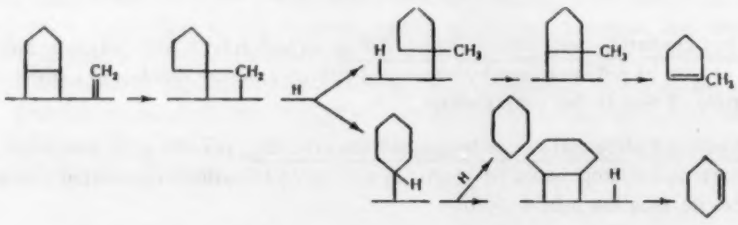
(5)

which, when they are dehydrogenated by the Zelinskii method are converted into toluene and o-dimethylbenzene, respectively, which may then be oxidized into benzoic and phthalic acids. Under similar conditions cyclopentene [10] will form a mixture of hydrocarbons of higher boiling point than the original cyclopentene, in a yield of 5% of the olefin and 33% of the carbon monoxide. After the mixture has been completely hydrogenated, the product contains the hydrocarbons indicated as the end products in the scheme below in the proportions stated. These are evidently formed from hydrocarbons resulting from methylation, ethylation, and propylation of the cyclopentenes.



(6)

The partial enlargement of the five-membered ring takes place only during the hydrogenation condensation itself [11]. It appears that there are formed from the cyclopentene adsorbed molecules of methylenecyclopentane which, in the one hand, are converted through methylcyclopentyl to methylcyclopentene, and, on the other hand, takes on an atom of hydrogen and isomerizes into the cyclohexyl radical (the semihydrogenated form of cyclohexene). The surface reaction can thus be represented as:



(7)

Under the same conditions cyclopentadiene yields mono-, di- and trimethyl derivatives in a yield of 5% [12].

If the straight chain aliphatic olefins are used, the homologization proceeds to a great extent, but is complicated by the simultaneous occurrence of hydrogenation-polymerization. Ethylene [13, 14] is methylated into propylene with a yield of 7-8%, while the reaction with propylene gives products containing 10% of hydrocarbons with four carbon atoms in the molecule [15]. Methylation of butene-1 gives C_5-hydrocarbons in a yield of 24%, half of this in the form of hydrocarbons of iso-structure [16]. Pentene-1 is methylated to hexene and hexane in a yield of 20%. As in the reactions involving the cycloolefins, the straight chain aliphatic olefins are alkylated through an active intermediate form which arises from the reaction with carbon monoxide.

This is confirmed by the results of an investigation by Fletcher and Gibson [17], using an isotope method, of the hydrogenation-condensation of ethylene. $C^{14}O$ marker, and the distribution of the radioactivity in the propylene formed was thus determined.

2. The Hydrogenation-Polymerization of Olefins

In distinction from the cycloolefins, olefins of the aliphatic series, in addition to undergoing hydrogenation-condensation, also participate in hydrogenation-polymerization, especially if the carbon monoxide content in the initial mixture does not exceed 5-7%. Both true polymers (that is, those whose composition is a direct multiple of that of the original olefin) and nonmultiple polymers are formed. In the hydrogenation-condensation of ethylene [13, 14], the products include butylenes and butane (20%), hexenes and hexanes (19%), octenes and octanes (13%), pentenes and pentanes (12%), heptenes and heptanes (16%), and nonenes and nonanes (9%). The hydrogenation-condensation of propylene [15] gives 20% of dimers (hexenes and hexanes), 11% of trimers (nonenes and nonanes), and 14% of C_5-hydrocarbons, 14% of C_7 and 15% of C_8. In the hydrogenation-condensation of butene-1, there are produced 15% of C_6-hydrocarbons, and 8-9% each of C_7, C_8 and C_9 [18]. Pentene-1 gives rise to 10% of C_7, 7% of C_8 and 10% of C_9 [19]. The hydrogenation-polymerization reaction in the presence of low concentrations of carbon monoxide and of hydrogen is not initiated by the carbon monoxide molecules themselves, but by the surface compounds formed through incomplete reduction of these. The number of molecules of the olefin entering into reaction in association with one reacting carbon oxide molecule is considerably greater than unity, and may sometimes reach the value of some tens, while increasing with reduction in the carbon monoxide concentration. These data suggest that the heterogeneous catalytic reaction should be considered as a radical-chain process [20].

The hydrogenation-polymerization of olefins, usually, goes very slightly or not at all in the absence of carbon monoxide. The reaction, like the hydrogenation-condensation reaction of carbon monoxide with olefins, seems to be linked with the incomplete reduction of the carbon monoxide, which points to the initiating role played by the active forms which arise as a result of this reduction.

It is interesting to note that the hydrogenation-polymerization of an ethylene-hydrogen mixture will proceed, not only under the influence of low concentrations of carbon monoxide in the gas mixture, but also under the effect of the residual active surface forms which are obtained through the interaction of the carbon monoxide, hydrogen and ethylene of that mixture. At first the catalyst is used for the hydrogenation-condensation reaction [21], and subsequently a mixture of ethylene and hydrogen containing no carbon monoxide is introduced. For some time the hydrogenation-polymerization of the latter mixture, from which carbon monoxide is absent, proceeds. Fletcher and Gibson [17] carried out these experiments using $C^{14}O$ as tracer in the preliminary hydrogenation-condensation and obtained similar results. They detected the presence of radioactivity both in the volatile and in the high-boiling fractions obtained as a result of the hydrogenation-polymerization of the ethylene-hydrogen mixture. They confirmed that the hydrogenation-polymerization of the mixture of ethylene and hydrogen will not proceed if there is no carbon monoxide present in the gaseous mixture. That is, the initiating role of the carbon monoxide, or, more accurately, the products of partial reduction of this, has been confirmed. In addition to this, it was noticed that after the reaction had been initiated under the influence of the small quantities of carbon monoxide, there was also a partial formation of compounds possessing no radioactivity, even though the initial carbon monoxide had been labelled with C^{14}. It seems that these compounds must be formed by means of carbon atoms proceeding exclusively from the initial ethylene. In the opinion of Roginskii [22] these facts cast some doubt on the theory of the initiating role of the carbon monoxide in this process. This view, however, is based on the assumption that hydrocarbons are formed only through chain growth, and ignores the effect of chain destruction. Fletcher and Gibson [17], noting the fact that all the fractions from C_4 to C_{10} showed molecular radioactivity which increased in linear fashion with increase in the number of carbon atoms in the molecule, that the yields of true multiple polymers of ethylene, except for butylenes and butanes, were negligible, and that the methane produced during the reaction had only small radioactivity, have suggested that there may be some dissociation of the ethylene into methylene radicals, and so a partial chain-growth without the participation of carbon monoxide, the ethylene itself being the source of the methylene radicals. Roginskii and Golovina [23] have obtained similar results. It has seemed to us that the question as to whether ethylene undergoes dissociation is disputable, and requires further investigation. Under the conditions stated, we have up to now been unable to detect dissociation either with ethylene alone or in its mixtures with hydrogen. The most rapid process appears to be the destructive hydrogenation of the higher molecular weight reaction products.

It is important to note that different authors attach different meanings to the concepts of initiation, and of initiator of the chain heterogeneous catalytic reactions. Thus, any substance in whose presence the reaction may commence – that is, which may enter into the composition of the primary complex – is sometimes called an initiator. Hence, ethyl alcohol [24], or ethylene [25], which will easily form the primary complex during the synthesis of higher hydrocarbons from carbon monoxide and hydrogen, may be called initiators of this reaction [22]. But it seems to us that the term should not be usedfor any substance whatever which may take part in forming the primary complex, but rather to the one only which promotes the reaction and brings it into being. Thus, under the conditions under which the hydrogenation-polymerization of ethylene takes place under the influence of small carbon monoxide concentrations, neither ethylene, nor its mixture with carbon monoxide or hydrogen, will undergo reaction. Therefore neither hydrogen, nor carbon monoxide nor ethylene itself, though they undoubtedly enter into the formation of the primary complex, is strictly speaking the initiator of the reaction. However, if 0.1% of carbon monoxide is added to a mixture of ethylene and hydrogen, the hydrogenation-polymerization reaction will commence. It may therefore be suggested with great probability that the initiating agent in this case consists of the products of partial reduction of the carbon monoxide. For the same reason it can be said that ethylene and its homologues, which are intermediate products in the Orlov-Fischer-Tropsch synthesis, shouldn't be considered the initiators of this reaction, as is sometimes found in the literature [26]. These olefins may indeed participate in forming the complexes which initiate the polymerization chain and also in the growth of the chain, but the true initiator is most probably the methylene radical, produced by the incomplete reduction of carbon monoxide.

In considering the mechanism of the growth of the hydrocarbon chains during the catalytic hydrogenation-condensation of carbon monoxide with olefins, the catalytic hydrogenation-polymerization of the latter under the influence of CO in presence of H_2, and also the synthesis of hydrocarbons from carbon monoxide and hydrogen, we must choose between the polymerization schemes proposed by Orlov [3], Fischer [4, 27], Craxford and Rideal [28], and Herington [29], on the one hand, and a condensation-dehydrogenation scheme similar to that proposed by Storch [6], on the other. As we have observed already, in the case of isosynthesis, the growth of the hydrocarbon chain apparently occurs according to both types of scheme [5]. For the usual synthesis on a cobalt catalyst we must express a preference for a polymerization scheme, since it has been shown [24, 25] by means of the isotope method that ethylene takes part in the formation of the primary complex more readily than ethanol if these compounds are added to the initial mixture of carbon monoxide and hydrogen. The polymerization schemes, such as the one proposed by Herington [29], are also to be accepted for the mechanism of hydrogenation-condensation of carbon monoxide with olefins. It is necessary to note that in hydrogenation-polymerization processes, in addition to the surface radicals formed by the reduction of the carbon monoxide, there are also taking part in the reaction alkyl radicals which arise from the incomplete hydrogenation of adsorbed olefin molecules (the half-hydrogenated forms of the olefins):

(8)

There is ground to believe that the surface alkyl groups also, in certain circumstances, may act as initiators for the polymerization of olefins. This would explain why sometimes the catalytic hydrogenation of olefins is accompanied by their polymerization or hydrogenation-polymerization. In our own experiments, under the conditions of the hydrogenation-polymerization reaction, a mixture of the olefin and hydrogen in the absence of carbon monoxide gave, in addition to the corresponding paraffin hydrocarbon, small amounts of the hydrogenation-polymerization products. The yield of this increases with increase in the molecular weight of the olefin, being zero for ethylene and 8.0% for hexene-1. These hydrogenation-polymerization processes were enhanced by the presence of carbon monoxide.

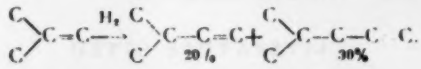
3. Destructive Hydrogenation, or Hydrogenation-Cracking

If we wish to explain all the complex chemical phenomena which arise both in hydrogenation-condensation and in hydrogenation-polymerization, as well as in the Orlov-Fischer-Tropsch reaction, it is impossible to limit the scheme simply to the question of chain growth [26], since chain destruction also plays an important part. It has already been noted by Craxford and Rideal [28] that hydrogenation-cracking plays a part in the synthesis of hydrocarbons from carbon monoxide and hydrogen. The essential part played in this process by the decomposition

of surface radicals have been pointed out earlier [30], when it was observed that chain growth alternates with chain destruction. Confirmation of this was provided convincingly by our experimental results, obtained recently for the hydrogenation-condensation and hydrogenation-polymerization of isobutylene.

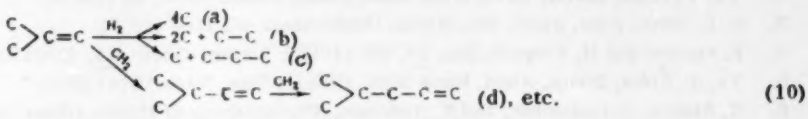
It has been shown that isobutylene [31], in the absence of carbon monoxide and hydrogen, polymerizes to a certain extent on a cobalt catalyst, but that the addition of as little as 0.2% of hydrogen doubles the yield of liquid polymerization products. The largest yield (up to 18% of the initial isobutylene) is obtained when the ratio of isobutylene to hydrogen is 1: 1.

In the hydrogenation-polymerization of isobutylene under the influence of hydrogen, but in the absence of carbon monoxide, the direction which the reaction takes depends on the ratio in which the reacting components are present [32]. When the ratio is isobutylene to hydrogen is 3: 1, the principal reaction is a true polymerization, with the production of diisobutylene, a smaller amount of triisobutylene, and their hydrogenation products; when the ratio is 1: 1 the reaction is greatly altered, and the products include a predominant amount of 2-methylalkanes and the corresponding olefins, such as 2-methylbutane, 2-methylpentane, 2-methylbutene and 2-methylpentene, of which these four make up 50% by volume of the liquid polymerizate:



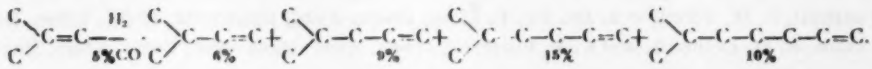
(9)

This unexpected direction of the reaction, which we have called destructive hydrogenation-polymerization of the isobutylene, indicates the origin of chain destruction. Additional investigation of the behavior of diisobutylene (2,4,4-trimethylpentene-1) under similar conditions has shown that, under the influence of hydrogen, it is not the dimer but the isobutylene itself which suffers destruction, which must be expressed in some such way as:



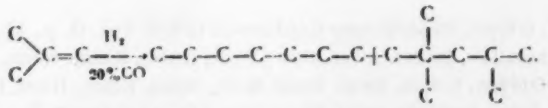
(10)

Addition of carbon monoxide to the mixture of isobutylene and hydrogen leads to a great increase in the yield of liquid hydrogenation-polymerization products, which may amount to 60% of the initial isobutylene [33]. If the carbon monoxide content is 5%, and the isobutylene: hydrogen ratio is 1: 1, this tendency of the reaction is maintained. The essential products are 2-methylalkanes and the corresponding olefins, but with higher molecular weights. Thus:



(11)

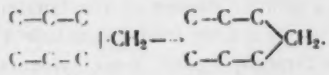
However, if the carbon monoxide content is increased to 20%, then, in the first place, the yield of the hydrogenation-polymerizate is diminished to 10%, and, in the second, the direction of reaction is greatly changed. After full hydrogenation of the liquid condensate, the products contain 33% n-heptane and 15% 2,2,4-trimethylpentane:



(12)

These results show that, in the presence of excess of hydrogen, isobutylene undergoes the homologization reaction, which is greatly enhanced by adding up to 5% carbon monoxide to the isobutylene-hydrogen mixture. The products of the incomplete hydrogenation of the carbon monoxide and of the destructive hydrogenation of the isobutylene react in one and the same direction. It is possible that there occur among the

intermediate products of these two reactions active surface forms of the same nature, such as the methylene radical. For high carbon monoxide contents in the initial mixture, both the hydrogenation and the hydrogenation-cracking are weakened, and in addition the isobutylene is to a considerable degree forced out of the adsorption layer on the catalyst. Part of it is converted into true multiple polymers, while another part is decomposed under the influence of the hydrogen according to reaction (10c), giving methylene radicals and other radicals containing three carbon atoms. At comparatively high concentrations of carbon monoxide, a large number of methylene radicals are formed from it. Under these conditions, the C_7 hydrocarbons predominate among the normal chain hydrocarbons produced, which is in excellent agreement with our earlier postulate [20] of a bridge scheme for the hydrogenation-polymerization of olefins:



(13)

These new experimental results reveal very graphically how great a part is played by chain destruction (together with chain growth) in the processes which have been considered.

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LIQUID-PHASE CONTACT-CATALYTIC OXIDATION OF ORGANIC COMPOUNDS ON NOBLE METALS

I. OXIDATION OF MONOPHENYL ETHER OF ETHYLENE GLYCOL TO PHENOXYACETIC ACID

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The contact-catalytic oxidation of the monophenyl ether of ethylene glycol has been studied. It has been established that on platinum catalysts in the liquid phase the monophenyl ether of ethylene glycol is oxidized selectively to phenoxyacetic acid by oxygen or by air under pressure. The conversion reaches 86%. Certain kinetic regularities have been studied.

The liquid-phase oxidation of organic compounds on noble metals by oxygen or oxygen-containing gases in a number of cases is characterized by good selectivity. The alcohol group of complex organic compounds is oxidized to aldehyde (ketone) or acid groups without changing other functional groups or the basic skeleton of the compound. The simpler alcohols are oxidized on platinum catalysts to the corresponding aldehydes and acids with good yields [1, 2, 3].

It is of interest to utilize liquid-phase oxidation on noble metals for the direct oxidative preparation of certain substances which are widely used in the organic synthesis industry, and which are being obtained by complex means because of the presence of reactive groups in the molecule which are not stable to oxidation under presently accepted industrial process conditions.

As the first of such objectives, we chose the reaction of oxidation of the monophenyl ether of ethylene glycol (phenoxyethanol) to phenoxyacetic acid; the present work is devoted to a study of this reaction.

Earlier, one of us [4] had established that the vapor-phase oxidation of phenoxyethanol to phenoxyacetic acid on vanadium pentoxide or silver proceeds with very low conversions.

EXPERIMENTAL

The atmospheric-pressure oxidation of phenoxyethanol by oxygen was carried out in aqueous medium at 90-97° in a four-necked flask equipped with a thermometer, reflux condenser, and mechanical stirrer. Elevated-pressure oxidation by air was carried out in a batch apparatus made of Kh18N9T steel, equipped with an electromagnetic stirrer (without packing gland), which made it possible to conduct the study at pressures up to 200 atm (Fig. 1). The use of dual apparatus permitted parallel experiments and checking the reproducibility of results. The volume of the apparatus is 75 ml, and the working volume 50 ml.

The catalysts tried for phenoxyethanol oxidation had various contents of platinum on several carriers: carbon (AG-2), pumice, α-alumina, aluminosilicate (USh), and silica gel (KSK of the Voskresensk Chemical

Combine). On carbon, pumice, and α-alumina the catalysts were prepared, according to methods given in [1], by the reduction of the platinum on the surface of the carrier by formalin in sodium carbonate medium. On aluminosilicate and silica gel the platinum was applied by impregnating with a solution of chloroplatinic acid in ammoniacal medium at 60-70°. After a 12-hour soaking the catalyst was filtered off, washed, dried, and reduced in a stream of hydrogen at 340-360° for 6 hr.

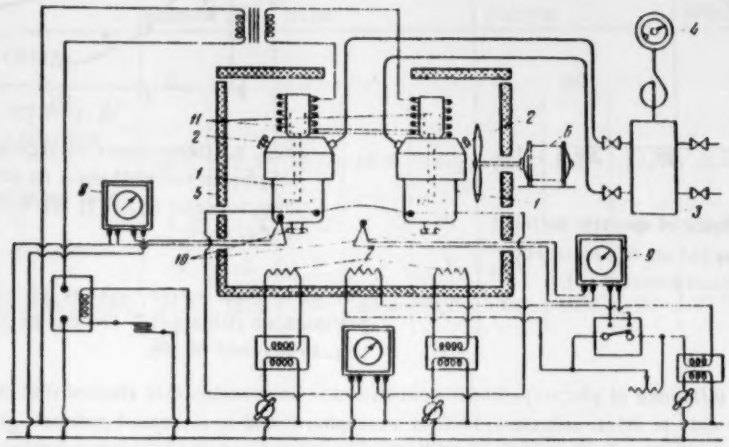

Fig. 1. Basic assembly diagram. 1) Apparatus for operation up to 200 atm pressure; 2) charging inlet; 3) air manifold and valves; 4) pressure gauge; 5) thermostat; 6) fan; 7) electrical heating system; 8), 9) electronic potentiometers; 10) discharging outlet; 11) electromagnetic stirrer.

The catalyzate (after hot filtration) was made alkaline with sodium carbonate solution, washed twice with small portions of ether for extraction of unreacted phenoxyethanol, acidified with hydrochloric acid, and extracted three times with portions of ether (15-20 ml). After evaporating off the ether, the obtained product (recrystallized from water) had a melting point of 96-97.5° (melting point of phenoxyacetic acid 96-98°), did not give any melting-point depression with phenoxyacetic acid obtained from phenol and chloracetic acid, and by elementary analysis corresponded to $C_8H_8O_3$.

Calculated %: C 63.15; H 5.36. Found %: C 62.88; H 5.33.

Besides phenoxyacetic acid, unreacted phenoxyethanol was found in the catalyzate (identified by refractive index), and also traces of an unidentified aldehyde. A test for formic and acetic acid gave negative results. Phenoxyacetic acid was determined quantitatively by alkaline titration (with phenolphthalein) of the unrecrystallized product, dried to constant weight after evaporation of the ether.

DISCUSSION OF RESULTS

As a guide for subsequent work, the initial study was aimed at determining the effect of pressure on the degree of conversion of phenoxyethanol to phenoxyacetic acid on platinum catalysts. The results of this study showed that pressure increases the reaction rate sharply (Table 1) and correspondingly increases the degree of conversion. Therefore, all subsequent experiments were conducted at 140 atm air pressure. An oxidation temperature of 140° was chosen on the basis of the results of preliminary experiments. In addition to platinum catalysts, other metallic and oxide catalysts were tried, as follows: Co, V_2O_5, MoO_3, and platinum-promoted Ni, Cu, and Co. These experiments were conducted at 140° and 140 atm for 3 hours. No phenoxyacetic acid was obtained on any of the platinum-free catalysts. With soluble catalysts (Mn acetate and resinate, Co stearate) no acid formation was observed. Accordingly, only the platinum catalysts were studied in more detail. It was established that the activity of platinum catalysts under comparable conditions is directly dependent on the specific surface area of the carrier (Fig. 2). More detailed data, obtained on catalysts with various carriers, are presented in Table 2.

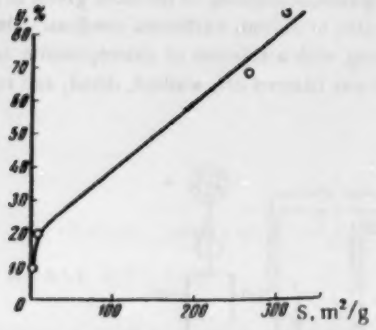

Fig. 2. Influence of specific surface area of carrier (S) on degree of conversion of phenoxyethanol (y).

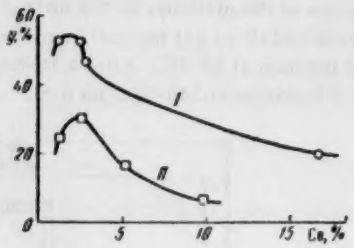

Fig. 3. Dependence of degree of conversion of phenoxyethanol upon its initial concentration in water (C_0): I) 8% Pt/carbon; II) 5% Pt/α-Al_2O_3.

The most active catalyst proved to be "10% platinum on silica gel." On this catalyst the conversion to acid reached 86.5%.

A study of the influence of phenoxyethanol concentration on reaction rate showed that the oxidation proceeds successfully only in dilute solutions, both at atmospheric and at increased pressure, giving maximum conversion at a phenoxyethanol concentration of 1.5-3% (Fig. 3). Increasing the phenoxyethanol concentration above 3% reduces the conversion markedly. At the higher concentrations the phenoxyethanol blocks the catalyst surface, hindering the access of oxygen to it, and thus deactivates the catalyst. This blockage is especially

TABLE 1

Oxidation of Phenoxyethanol on 8% Pt/Carbon Catalyst (Quantity of catalyst 2-2.5 g in 100 ml of reaction solution. Initial concentration of phenoxyethanol 1.5-2.5%, temperature 100°)

	Pressure					
	1 atm			10 atm		
Duration of experiment, hr	5	9	30	2	3	5
Conversion of phenoxyethanol to phenoxyacetic acid, %	14.5	17.0	25.0	48.7	55.0	41.7

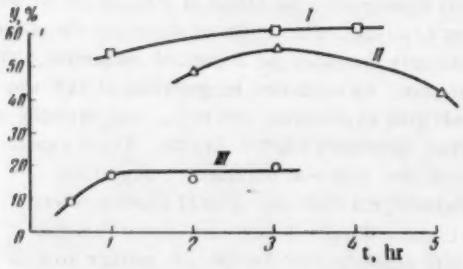

Fig. 4. Dependence of degree of phenoxyethanol conversion upon duration of experiment: I) 5% Pt/aluminosilicate; II) 8% Pt/carbon; III) 5% Pt/α-Al_2O_3.

effective in the presence of undissolved phenoxyethanol. The curves of phenoxyethanol conversion vs reaction time demonstrate the resistance of the formed phenoxyacetic acid to oxidation under the conditions studied and also the high selectivity of the platinum catalysts, the action of which is limited entirely to the oxidation of the alcohol group to carboxyl. Some reduction of yield of phenoxyacetic acid upon prolonged oxidation was observed only on the "platinum on carbon" catalyst (Fig. 4).

SUMMARY

1. Feasibility has been established for the liquid-phase contact-catalytic oxidation of phenoxyethanol to

TABLE 2

Oxidation of Phenoxyethanol to Phenoxyacetic Acid on Platinum Catalysts (temperature 140°, pressure 140 atm)

	Catalyst									
	5% Pt on pumice		5% Pt on α-alumina			5% Pt on alumino-silicate			10% Pt on silica gel	
Specific surface, m^2/g	0,5–1,3		9,8			264			312	
Catalyst quantity, g/100 ml of reaction solution	12,5	12,5	12,5	18,5	12,5	6,2	6,2	12,5	2,5	12,5
Phenoxyethanol conc. in water, %	1,35	5,25	5,25	5,25	10	1,35	2,7	2,7	2,7	2,7
Duration of experiment, hr	2	2	1	1	1	3	3	3	3	3
Degree of conversion, %	29,6	17,9	17	22,6	6,7	61	45	68	36,8	86,5

phenoxyacetic acid (with yield up to 85%) on platinum catalysts by oxygen at atmospheric pressure or by air at increased pressure.

2. A study has been made of the influence of various kinetic factors on the rate of this oxidation.

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STRUCTURE AND TEXTURE OF ALUMINUM – CHROMIUM – POTASSIUM CATALYSTS AND THEIR ACTIVITY AND SELECTIVITY IN THE DECOMPOSITION OF i-C_3H_7OH

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There have been determined the phase composition, structure, and texture of impregnated aluminum–chromium–potassium catalysts with 3-33 wt. % of Cr_2O_3 and 0.5-5.9% of K_2O, and also values of their total and specific activity and selectivity coefficient at 320-350° in the reactions of decomposition of absolute i-C_3H_7OH. Data were obtained on the comparative activity of solid solutions of the components, which have spinel and corundum structures. On the basis of data indicating a dynamic equilibrium between the phases containing K^+ ions (depending on the oxidation-reduction conditions of the medium), a hypothesis has been advanced regarding the chemical composition of the surface of the catalysts and the distribution of components in them.

As is well known, Al_2O_3–Cr_2O_3 catalysts have proved to be extremely valuable for carrying out the reactions of dehydrocyclization (aromatization) and dehydrogenation of paraffins. There are also a number of other possibilities for utilizing these catalysts, which are described in sufficient detail in the review literature [1, 2].

Research on the physical structure of aluminum–chromium catalysts has presented substantial difficulties; however, in the recent works of Griffith and others [3-7] this problem was worked out successfully. A significant contribution to the characterization of the physical properties of aluminum–chromium catalysts was made by the work of Eishens and Selwood [8, 9]. Interesting results were obtained very recently by Lyubarskii and Ermakova [10], who studied the adsorption properties of impregnated aluminum–chromium catalyst (for the dehydrogenation of hydrocarbons) containing about 10% chromic oxide. They found that the thermal stability and degree of carbon deposition are related to the degree of purity of the original aluminum oxide and to its pore structure; the presence of alkali reduces stability. High-temperature treatment effects enlargement of the pores and a decrease of carbon deposition. Calcination at temperatures below 750°, although it is also accompanied by a decrease of surface, has little effect on catalyst activity. In this same work it was demonstrated that above 1 mm the size of catalyst grain has an effect on the depth of conversion, but below 1 mm there is no effect.

An intrinsic disadvantage of aluminum–chromium catalysts is their relatively rapid decrease of activity and the short operating cycle up to regeneration. It has been demonstrated [11] that Al_2O_3–Cr_2O_3–K_2O dehydrogenation catalysts are more stable and more selective in their action. The characteristics of their phase composition, texture, and structure thus far have not been described. The determination of these properties was the subject of the present study. At the same time we intended to ascertain to what extent these catalysts show the dehydrating qualities of Al_2O_3 and the dehydrogenating ability of Cr_2O_3. It is easiest of all to follow selectivity of action in the decomposition reactions of an alcohol. Here we report results of a study with isopropanol.

*Catalysts were prepared by O. D. Sterligov and A. P. Belen'ka.

It should be noted that up to now no information has appeared in the literature on the specific catalytic activity [12] of aluminum–chromium or aluminum–chromium–potassium catalysts. This characteristic, expressed in the form of the activity of 1 m^2 of catalyst surface, permits (in contrast to other methods of evaluating activity) an objective comparison among catalysts of a given group. In this work we determined the specific activity of aluminum–chromium–potassium catalysts of varying composition in the dehydrogenation and dehydration of isopropanol, and also the effect of adding K_2O upon the specific activity of Al_2O_3 and Cr_2O_3.

EXPERIMENTAL

1. Objectives of Investigation

Catalysts were prepared by impregnating the Al_2O_3 and subsequent calcination in air at 550°. They differed in content of the components: in the basic series of samples A_1–A_9 the ratio Cr_2O_3: K_2O was constant, and the ratio Al_2O_3: (Cr_2O_3 + K_2O) was varied. In the samples A_{10}–A_{14} the K_2O content was varied with approximately constant ratio Al_2O_3: Cr_2O_3. Finally, samples of Al_2O_3 + K_2O and Cr_2O_3 + K_2O were prepared; a study of these materials was found necessary to establish the influence of K_2O on the selectivity of the catalyst components. The composition of the basic series of samples investigated, A_1–A_9, together with values of specific surface area and characteristic porosity, is listed in Table 1. For the remaining catalyst samples, these data are listed in other tables along with data on catalytic activity. The residual water content of the catalysts was determined by calcining weighed samples at 1000-1100° to constant weight.

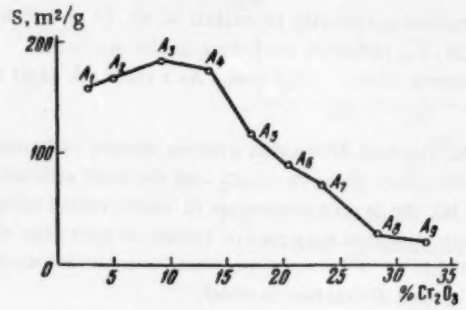


Fig. 1. Variation of specific surface area with catalyst composition.

2. Specific Surface, Specific Pore Volume, and Average Pore Diameter of Catalysts

Determination of values of specific surface S, specific pore volume V, and average pore diameter d was carried out by measuring adsorption of benzene vapor at 20° by a dynamic method which we described previously [13]. The catalyst sample weights were 2-3 g. The values of S were calculated from four points of the adsorption isotherm within the limits of p/p_s from 0 to 0.356, using the BET equation. Selected control determinations under static conditions in vacuum equipment (also by adsorption of C_6H_6 vapors at 20°) gave values in good agreement with the results of the dynamic-method determinations.

TABLE 1

Composition, Specific Surface S, Total Pore Volume V, and Average Pore Diameter d of Catalysts A_1–A_9

Catalyst	Content, wt. %			Residual H_2O	S, m^2/g	V, cm^3/g	d, Å
	Al_2O_3	Cr_2O_3	K_2O				
A_1	97,0	2,6	0,5	2,4	158(153)	0,25	63
A_2	94,0	5,0	0,9	2,6	168(179)	0,25	60
A_3	88,9	9,4	1,7	2,0	183(165)	0,21	45
A_4	84,2	13,5	2,4	1,6	175(158)	0,16	38
A_5	80,0	17,0	3,1	1,2	117(147)	0,12	40
A_6	76,0	20,3	3,7	1,9	90 —	0,12	52
A_7	72,5	23,3	4,2	1,5	73 (76)	0,11	60
A_8	66,6	28,3	5,1	2,2	28 (32)	0,04	62
A_9	61,5	32,6	5,9	1,5	21 (34)	0,04	83

The specific pore volume V was determined by the amount of adsorption of C_6H_6 vapors at 20° with p/p_s near to 1.0. The average pore diameter was calculated on the basis of the simplified equation $d = 4V/S$.

As is evident from the data of Table 1 and Fig. 1, the values of S in the series A_1-A_9 show a marked variation with the Cr_2O_3 content of the catalysts. At first, S increases slightly and passes through a maximum at about 10% by weight of Cr_2O_3 (and 1.7% K_2O); beginning with 13-14% Cr_2O_3 the value of S decreases rapidly and at A_9 has fallen almost to one-ninth of the maximum value. The specific pore volume V also decreases with an increase of Cr_2O_3 content, becoming very small at A_9 (one-sixth of the value at A_1 or A_2). The average pore diameter does not vary markedly; it passes through a minimum at A_4-A_5, in the region of which d nevertheless remains sufficiently large that rather large molecules can penetrate into the pores. The values of S shown in parentheses in Table 1 are for the catalysts used in experiments on the decomposition of $i\text{-}C_3H_7OH$. A comparison of the values of S for fresh and used catalysts shows that their difference is within the limits of error of the determination and that S is practically unchanged under the conditions of the experiments.

3. Phase composition and structural characteristics of catalysts from electron and x-ray diffraction data

Electron diffraction patterns were obtained on an ÉM-4 electronograph with potentials of 33, 39 and 45 kv. X-ray diffraction patterns were photographed with filtered (Ni) Cu, K_α radiation according to the method of Straumanis with assymetric placement of the film in a Debye camera with d = 57.3 mm. As a standard, MgO was introduced into the sample for photographing.

TABLE 2

Values of Lattice Parameter of Spinel Phase in Catalysts A_1-A_9 from Electron and X-ray Diffraction Data

Catalyst		a, Electron diffraction, A	a, X-ray diffraction, A
No.	% Cr_2O_3		
A_1	2,6	7,852	
A_2	5,0	7,863	7,700
A_3	9,4	7,873	7,724
A_4	13,5	7,887	7,792
A_5	17,0	7,889	7,834
A_6	20,3	7,900	7,888
A_7	23,3	7,909	7,916
A_8	28,3	7,906	7,920
A_9	32,6	7,918	7,928

The electron diffraction patterns showed reflections of only the spinel phase (γ-Al_2O_3 and the solid solution of Cr_2O_3 in it), the lattice parameter of which varied with Cr_2O_3 content within very narrow limits, as seen from the data of Table 2. The corundum phase was not detected by the electron diffraction method.

X-ray diffraction likewise detected only the spinel phase in catalysts containing up to 20% Cr_2O_3. At higher Cr_2O_3 contents the corundum phase appeared, consisting of α-Al_2O_3, Cr_2O_3, and their solid solutions. To ascertain whether a crystalline AlOOK phase was present, we prepared* the corresponding compound and photographed its x-ray diffraction pattern for comparison with the patterns of the catalysts. However, this was not successful in settling the question of the presence of this phase, since in the diffraction patterns of the catalysts with sufficiently high content of K the two most intense lines of AlOOK (d = 2.63 and 2.20 A) are covered up by the reflections of the corundum phase. The presence of K_2CrO_4 in the original and regenerated catalysts was confirmed by other methods; however, it could not be detected successfully by the x-ray method: this substance occurs in the catalysts in the amorphous state.

The x-ray-determined values of lattice parameter of the spinel phase varied within wider limits than did the values determined by electron diffraction.

*The preparation of this compound was carried out by obtaining the compound $K_2[Al_2O(OH)_6]$ according to directions contained in the book "Handbuch der Preparativen Anorganischen Chemie," Herausgegeben G. Brauer, Stuttgart, 1954 (Russian translation, IL, 1956, p. 770), and calcining this compound at 500°, upon which it lost water and approached the composition AlOOK.

4. Magnetic Measurements

Measurement of the magnetic susceptibility of the catalysts was carried out by the Faraday method at 23, 80, and 160° with field intensities in the interval of 2000-5000 e, in an apparatus with a microbalance of 0.00001 g sensitivity. The magnetic susceptibility of Al_2O_3 was measured according to Gouy. The magnetic susceptibility of χ of the catalysts was measured with accuracy ± 2.5%, the Weiss constant Δ was determined with accuracy ± 10°, and the magnetic moment μ with accuracy in the order of ± 0.1 μ_B.

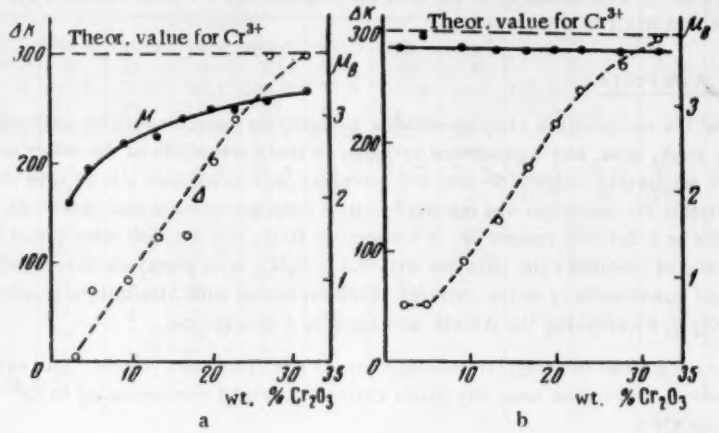


Fig. 2. Dependence of Δ and μ on the composition of aluminum–chromium–potassium catalysts: a) Series A before use; b) series A after use.

The magnetic susceptibility of the original Al_2O_3 at 20° proved to be equal to $-0.11 \cdot 10^{-6}$. It was independent of field intensity, but decreased slightly with temperature: at 80° it was $-0.15 \cdot 10^{-6}$, and at 160° it was $-0.16 \cdot 10^{-6}$. This indicated the presence of traces of ferromagnetic oxides (probably iron oxides). However, these oxides were present in the form of a solid solution, so that their reduction at the temperatures of the catalytic experiments was hindered (such reduction might alter the results of the determinations); therefore, it proved feasible to carry out the usual magnetic-chemical study, introducing a correction for the diamagnetism of Al_2O_3. The results of such determinations are shown in Table 3, and the corresponding calculated values of

TABLE 3

Magnetic Susceptibility of Catalysts, $\chi \cdot 10^6$

Catalyst		$\chi \cdot 10^6$ (initial catalysts) at temperature			$\chi \cdot 10^6$ (used catalysts) at temperature		
№	% Cr_2O_3	23°	80°	160°	18°	83°	160°
A_1	2,6	0,51*	0,41	0,30	1,6	1,3	1,1
A_2	5,0	1,27**	1,00	0,84	3,8	3,2	2,8
A_3	9,4	3,0	2,5	2,2	5,3**	4,7	4,1
A_4	13,5	4,4	3,8	3,3	7,0**	6,0	5,3
A_5	17,0	6,0	5,1	4,5	7,9**	7,0	6,2
A_6	20,3	6,4	5,7	5,0	8,6	7,4	6,9
A_7	23,3	7,3	6,4	5,6	9,2	8,0	7,2
A_8	28,3	8,2	7,2	6,4	10,7	9,5	8,5
A_9	32,6	9,9	8,2	7,35	11,9	10,7	9,6

*Measured at 18°.

**Measured at 20°.

Δ and μ in Fig. 2. The values of μ of the original catalysts (Fig. 2a) lie significantly below the value of μ for the Cr^{3+} ion. This is undoubtedly connected with their significant content of Cr^{6+}. For catalysts with low Cr_2O_3 content the values of μ are reduced more than for catalysts with high Cr_2O_3 content, evidently because of the greater proportion of Cr^{6+} contained in A_1-A_3.

After the catalytic experiments (Fig. 2b) the value of μ was the same for all samples, approximately equal to 3.6 μ_B, but remained lower than for Cr^{3+}. Hence it is concluded that the used catalysts also contain a certain residual quantity of Cr^{6+}. The values of Δ for both the original and the used catalysts increase monotonically with increasing content of Cr in the catalysts.

5. Chemical Analysis

To determine the composition of water-soluble components (which could be assumed to be AlOOK, CrOOK, and K_2CrO_4) of the fresh, used, and regenerated catalysts, a study was made of the water extracts obtained by repeated boiling of accurately weighed 2- and 3-g samples (each extraction was 10 min with 50 ml of H_2O; in the case of colored extracts the operation was repeated until a colorless extract was obtained). The extract thus obtained was diluted to a definite volume in a volumetric flask, and aliquots were taken for determination of Cr^{6+} (iodometric) and of alkalinity (by titration with 0.1 N H_2SO_4 with phenolphthalein indicator). In addition, Al^{3+} was determined quantitatively in the extract: 1) by reaction with alcoholic alizarin-red solution, and 2) by the action of NH_4Cl, hydrolyzing the AlOOK and forming a precipitate.

The water extracts from the original and regenerated catalysts were yellow. The extracts from the used catalysts were colorless; in no case were any green extracts obtained corresponding to Cr^{3+} (for example, in the form of chromite, CrOOK).

The Cr^{6+} content in the extracts from the original catalysts A_1, A_2, A_4, A_5, A_7, A_8, A_{10}, and A_{11}* proved to be equal to 0.67, 1.45, 1.73, 2.07, 2.86, 3.68, 1.96, and 1.60% respectively. This corresponds to K_2CrO_4 contents of 2.35, 5.40, 6.45, 7.75, 10.8, 13.7, 7.3, and 6.0%. As shown by these data, the Cr^{6+} content in the original catalysts does not increase in proportion to their total Cr content. In the Cr-poor catalysts A_1 and A_2 the proportion of Cr^{6+} is considerably greater than in the Cr-rich catalysts. Thus, the chemical analyses agree well with the magnetic data.

Of the samples used in the catalytic experiments, only A_8 showed traces of Cr^{6+} in the water extract; the others did not contain measurable amounts of Cr^{6+}. Since the magnetic data indicated the presence of Cr^{6+} in the used catalysts, it may be concluded that the Cr^{6+} was in the interior volume of the crystallites and not on their surfaces, and hence was not extracted.

All of the original and regenerated catalysts gave a neutral reaction, but the extracts of the used catalysts were alkaline. This circumstance is used below as the basis for reasoning on the K^+ ion contents of the catalyst phases. It should be noted that the used catalysts could never be washed to neutral reaction of the extract. Therefore, the total alkali content could not be determined. However, this did not have a serious effect from the point of view of determining the K^+ content of the components or phases of the catalysts. As an example of the determinations conducted, we cite results obtained with A_4. After it had been used in the catalytic reaction for 30 minutes, its extract contained a quantity of KOH equivalent to 1.7 ml of 0.1 N solution per gram of catalyst, and after 6-hour use the extract KOH equivalent was 2.2 ml of 0.1 N solution per gram of catalyst. Thus, the degree of reduction of the Cr^{6+} contained in the catalysts apparently was significant, and influenced to some extent the alkalinity of the extract.

6. Tests of Catalyst Activity

Activity of the catalysts was determined by the decomposition of absolute isopropanol in a flow system with constant catalyst volume in all experiments (2 ml). Granular catalyst (approx. 1 mm) was selected so that diffusion factors would not influence the kinetics [10]. The basic experiments were conducted at 320-350° in 15° intervals with volume rate 2.3 hr^{-1}, and supplementary experiments at 3.5 and 7.0 hr^{-1} and also at 500°, i.e., at a temperature near the accepted temperature for dehydrogenation of paraffins. The temperature of the electric

*Only small quantities of A_3, A_6, and A_9 remained after the catalytic experiments; therefore their extracts were not analyzed for Cr^{6+}.

TABLE 4

Decomposition of i-C_3H_7OH on Catalysts A_1-A_9

Catalysts	Volume rate 2,3 hr^{-1} 320° C_3H_6	H_2	335° C_3H_6	H_2	350° C_3H_6	H_2	3,5 hr^{-1} 350° C_3H_6	H_2	2,3 hr^{-1} 500° C_3H_6	H_2	7,0 hr^{-1} 500° C_3H_6	H_2
A_1	85,5	20,0	141,3	26,9	180,0	32,0	138	23				
	29	7	43	9	62	11	42	8				
A_2	44,9	30,8	70,6	49,1	109,0	56,1	75,9	43,9	128,8	180,0		
	15	11	24	17	37	19	26	15	43,8	61,0		
A_3	20,4	74,5	25,8	77,6	44,7	104,3	133,5	88,4				
	7	25	9	26,4	15	35	11	30				
A_4	9,0	53,0	14,1	73,7	17,4	82,1	14,3	73,4	47,0	250,0	42,5	251,0
	3	18	5	25	6	28	5	25	16,1	85	14,5	85,5
A_5	7,0	74,8	9,0	90,3	10,6	103,3	7,9	83,4				
	2,4	25	3,1	31	4	35	2,5	28				
A_6	4,1	67,1	5,1	83,9	6,4	97,0	3,2	65,3				
	1,5	23	1,7	29	2	33	1	22				
A_7	2,9	61,0	3,1	68,5	4,5	85,0	3,0	64,5	38,5	262,0		
	1	21	1	23	1,5	29	1	22	13	90		
A_8	1,7	33,5	1,7	33,5	1,8	38,0						
	0,5	11	0,5	11	0,5	13						
A_9	1,1	20,0	—	18,0	—	24,0						
		7		6		8						

TABLE 5

Values of Rate Constants of Dehydrogenation and Dehydration of Isopropanol, $k \cdot 10^4$, moles · min^{-1}

Catalysts	Volume rate 2,3 hr^{-1} 320° C_3H_6	H_2	335° C_3H_6	H_2	350° C_3H_6	H_2	3,5 hr^{-1} 350° C_3H_6	H_2	2,3 hr^{-1} 500° C_3H_6	H_2
A_1	3,26	0,7	6,1	0,94	8,4	1,12	8,9	1,3		
A_2	1,6	1,0	2,6	1,9	4,4	2,04	4,6	2,4	5,6	8,4
A_3	0,7	2,8	0,9	3,0	1,6	4,2	1,9	5,6		
A_4	0,3	1,9	0,5	2,8	0,6	3,2	0,8	4,4	1,7	15,0
A_5	0,25	2,8	0,35	3,5	0,36	4,1	0,5	5,15		
A_6	0,15	2,5	0,17	3,2	0,2	3,8	0,16	3,8		
A_7	0,1	2,2	0,1	2,5	0,15	3,34	0,1	3,8	1,4	15,3
A_8	0,05	1,2	0,05	1,2	0,06	1,3				
A_9	—	0,7	—	0,6	—	0,8				

furnace block was controlled to± 0,5° by an electronic controller; temperature was measured by a thermocouple introduced into the center of the catalyst bed. Measurement of reaction rate was always carried out 30 minutes after starting the alcohol feed to the catalyst. Preliminary experiments demonstrated that with 2 ml of catalyst in a U-shaped reactor this time interval was sufficient to establish steady gas evolution; i.e., stabilization of catalyst activity and composition under the conditions of experiment had been attained.

The rates of each of the parallel reactions in the decomposition of absolute isopropanol was judged by the volume of evolved gas (converted to STP) measured during the experiment at definite time intervals, and by the gas composition, determined in a VTI apparatus. From these data the degrees of conversion and rate constants of both reactions were calculated. The data in subsequent tables and figures for dehydration are designated as C_3H_6 or by this index, and the data for dehydrogenation as H_2 or by this index.

a) Basic series of catalysts. In Table 4 each of the upper figures represents the volume (STP) of C_3H_6 or H_2 produced from 1 ml of i-C_3H_7OH feed, and the lower figure represents the corresponding degree of conversion (in %) in the given reaction. The data of the table indicate that as the Cr_2O_3 and K_2O contents are increased the dehydrogenating activity increases rapidly (up to A_3) and then varies only slightly with composition (up to A_7). The dehydrating activity decreases as the content of these components increases, at first rapidly and then slowly but continuously. It should be noted that in the experiments at 500° pyrolysis occurred to a slight degree, as evidenced by contents of 3.7-5.0% CO_2 and 9-12% CH_4 in the gas. As a result of this pyrolysis, the sum $H_2 + C_3H_6$ exceeded 100% in the experiments at 500°.

Calculation of the reaction rate constants (Table 5) from the experimental data was carried out using the equation of Balandin and Bork [14] for reactions in a flow system:

$$k = \frac{N \cdot m}{M - m/2},$$

where N is the number of moles of feed per unit time, M is the number of ml of gas (STP) corresponding to 100% conversion of N in the given reaction, and m is the number of ml of gas actually evolved (C_3H_6 or H_2, respectively). For the decomposition of alcohol on A_1, $k_{C_3H_6} >> k_{H_2}$; with the catalyst A_2 the difference between these values is considerably less; and beginning with catalysts A_3, k_{H_2} becomes larger than $k_{C_3H_6}$, this difference being greater at higher contents of Cr_2O_3 and, correspondingly, of K_2O.

It is further seen from Table 5 that the rate constants of each of the reactions show little variation between volume rates of 2.3 and 3.5 hr^{-1}, and consequently the deviation might be explained by certain minor variations in experimental conditions; for example, slight pulsation of the alcohol feed, etc. At high degrees of conversion the difference between the rate constants (for 2.3 and 3.5 hr^{-1}) increases. This occurs because the Balandin-Bork equation is an approximation which, strictly speaking, is applicable only at low conversions.

b) Supplementary Experiments. To clarify the mutual influence of the catalyst components, we prepared the compounds indicated in Tables 6 and 7. As seen from the data of Table 6, the addition of 0.5% K_2O causes a sharp increase of the specific surface of the Al_2O_3 and a correspondingly marked increase of the degree of conversion in the dehydration of i-C_3H_7OH. A further increase of K_2O content leads to a sharp decrease of the degree of conversion in dehydration. No H_2 was detected in the reaction products in any of these experiments.

TABLE 6

Effect of K_2O Addition Upon the Activity of Al_2O_3 and Cr_2O_3 in the Decomposition of i-C_3H_7OH

Catalyst composition, wt.%		Apparent density, g/cm³	Residual H_2O, %	S, m^2/g	Degree of conversion at 350° and 2.3 hr^{-1}		$k \cdot 10^4$, moles·min^{-1}	
					C_3H_6	H_2	C_3H_6	H_2
Al_2O_3	K_2O							
100	0	0,75	2,5	175	74	0	10,7	—
99,5	0,5	0,75	1,2	360	93	0	16,5	—
97,0	3,0	0,75	0,9	300	11,2	0	1,1	—
94,0	6,0	0,70	2,8	146	7,4	0	0,7	—
Cr_2O_3	K_2O							
100	0	0,9	0,6	16	30,4	24,3	3,2	2,5
99,0	1,0	0,75	0,4	~1	0,02	5,7	0,02	0,5
95,0	5,0	0,70	0,4	~1	0,03	6,5	0,03	0,62
90,0	10,0	0,6		~1	0,03	6,8	0,03	0,65
85,0	15,0	0,6		~1	0,04	10,0	0,04	0,97

TABLE 7

Effect of Quantity of Added K_2O Upon Catalyst Activity [Activity expressed in ml (STP) of C_3H_6 and H_2 formed from 1 ml of absolute i-C_3H_7OH with volume rate 2.3 hr^{-1}.

Catalyst	K_2O, %	Residual H_2O, %	Apparent density	S, m^2/g	Reaction at 320°		335°		350°		375°	
					C_3H_6	H_2	C_3H_6	H_2	C_3H_6	H_2	C_3H_6	H_2
A_{12}	0,5	1,4	1,18	137	13,5	65,3	25,3	84,1	40,8	104	62,8	112,8
A_{10}	1,0	1,0	1,2	125	5,5	61,1	9,5	85,7	13,1	108	22,1	147,7
A_{11}	2,0	1,2	1,2	123	9,6	77,4	12,1	88,8	16,2	106,9	26,2	149
A_{14}	3,0	1,1	1,18	118	7,2	76,4	9,5	85,7	12,8	104,2	20,9	144,4
A_{13}*	10,0	1,7	1,35	50	2,0	33,4	2,3	37,5	2,4	41,1	3,4	57,6

* $Al_2O_3 : Cr_2O_3 = 70 : 20$.

The addition of K_2O to Cr_2O_3 reduces markedly the total degree of conversion ($C_3H_6 + H_2$), at the same time affecting the selectivity: the dehydrating activity is depressed much more sharply than the dehydrogenating activity. The degrees of conversion are low, which is apparently related to the fact that in our experiments the addition of K_2O led to a significant reduction of specific surface.

Table 7 incorporates data obtained with catalyst preparations in which $Cr_2O_3 : Al_2O_3$ ratio was practically constant (excluding A_{13}). The values of specific surface of $A_{10}-A_{12}$ and A_{14} coincide within the limits of error of the determination. The data on activity show that increasing the catalysts' K_2O content from 0.5 to 3.0% leads to some increase of total degree of conversion in the alcohol decomposition, the dehydration being suppressed and the dehydrogenation intensified. With further increase of K_2O content the over-all conversion and the degree of dehydrogenation are decreased, and the degree of dehydration remains at its previous, very low level.

DISCUSSION OF RESULTS

1. Phase Composition of Catalysts

A primary use of the obtained data is the determination of the phase composition of the investigated catalysts in the various stages of their existence. The analysis of the water extracts from fresh, used, and regenerated catalysts gives obvious evidence that the phase compositions are not identical. The original catalysts contain a great deal of Cr^{6+}, which remains only in very small quantity in the [internal] volume of the solid phase of the used catalysts. The alkaline reaction of the water extracts from the used catalysts and the presence of Al ion in these extracts is convincing evidence of the presence of potassium aluminate in them. The neutral reaction of the water extracts from the original and regenerated catalysts and the absence of Al ion indicates that potassium aluminate is not present in these solutions. In no case did we detect potassium chromite. On the other hand, the original and regenerated catalysts do contain potassium chromate, which is practically absent (it is not extracted by water) in the used catalysts. All of this leads to the conclusion that the K-ion-containing phases exist in a dynamic equilibrium which depends on the conditions (reducing or oxidizing) of the medium and which is displaced far in either direction for each of the given conditions. The topochemical reaction which takes place may be represented by the following schemes:

$$1.\ 2K_2CrO_4 + 2Al_2O_3 \underset{+3O}{\overset{+3H_2,\ -3H_2O}{\rightleftharpoons}} 4AlOOK + Cr_2O_3.$$

$$2.\ K_2CrO_4 + 3H \rightarrow CrOOK + KOH + H_2O;$$

$$Al_2O_3 + H_2O \rightleftarrows 2AlOOH,$$

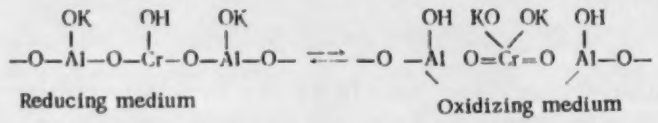
$$AlOOH + CrOOK \rightleftarrows AlOOK + CrOOHand2CrOOH \rightleftarrows Cr_2O_3 + H_2O;$$

$$AlOOH + KOH \rightleftarrows AlOOK + H_2O.$$

and in an oxidizing medium:

$$2AlOOK + \frac{1}{2}Cr_2O_3 + 1{,}5O \rightarrow Al_2O_3 + K_2CrO_4.$$

All of the indicated conversions are facilitated by the catalysts' containing a certain quantity of "residual water," i.e., they already have a certain quantity of hydroxides, including AlOOH and CrOOH. Potassium chromite in a reducing atmosphere either is not formed at all (1), or if formed (2) reacts rapidly with AlOOH giving AlOOK and CrOOH. In the reduced state the catalysts contain AlOOK, as the acidity of AlOOH exceeds the acidity of CrOOH. The extremely great ease of migration of the K^+ ion from Al to Cr (and back) in a solid substance is explained by the fact that the oxides of these metals form solid solutions; this follows from the analysis of the $Al_2O_3-Cr_2O_3$ system given in [7] and from the data which we obtained for $Al_2O_3-Cr_2O_3-K_2O$ catalysts. Arising from the assumption that the catalyst surface is hydrated, even partially, the following representation can be made of isolated fragments of the catalyst surface where the K^+ ion is exchanged between aluminate and CrOOH:



The proposed scheme agrees well with the fact that the introduction of K_2O into $Cr_2O_3-Al_2O_3$ catalysts suppresses dehydration: the replacement of H in AlOOH by K should hinder the intermediate formation of aluminum alcoholate, which also was shown by direct experiments (see Table 6). It should be added that they confirm the mechanism of dehydration through the alcoholates. Further, although the initial and regenerated catalysts contained potassium chromate, it was not detected as a crystalline phase in any of the samples. This agrees with what was stated above regarding the K-ion-containing phases: the ease of its migration attests to the molecular distribution of potassium chromate in the substance of the catalyst.

By x-ray diffraction we detected the spinel and corundum phases in all stages of treatment of the catalysts studied. The variation of lattice parameter of the spinel phase in the used catalysts, calculated according to the [004] and [044] reflections from x-ray and electron diffraction data, shows that this phase represents a solid solution of Cr_2O_3 in Al_2O_3: the lattice parameter increases with increasing Cr content in catalysts A_1-A_5 (i.e., up to about 20% Cr_2O_3) and does not vary further. This agrees well with data obtained by Davis, Griffith, and March [7]. Thus we may state that the introduction of K_2O into the catalysts did not change the $Cr_2O_3-Al_2O_3$ concentration ratio in the solid solution. However, in contrast to the cited work, we were not successful in detecting a η-phase; we dealt with the γ-phase of Al_2O_3 and solid solutions of Cr_2O_3 in it. It is possible that this was caused by the fact that we started with the preparation of catalysts from γ-Al_2O_3.

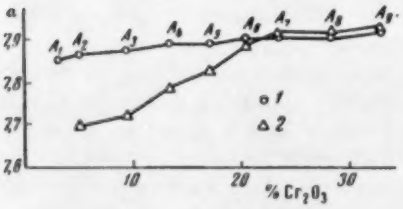


Fig. 3. Lattice parameters of γ-phase in catalysts A_1-A_9: 1) Electron diffraction data; 2) x-ray diffraction data.

As seen from Fig. 3, the electron and x-ray diffraction data are not identical as to the rate of variation of lattice parameter of the spinel phase with catalyst composition. The electron diffraction values of a for A_2-A_5 are larger than those determined by x-ray diffraction, whereas for A_6-A_9 (i.e., in the region of saturated solid solution of Cr_2O_3 in γ-Al_2O_3) they practically coincide. Precisely the latter circumstance indicates that the observed deviations are not accidental and are not differences in accuracy of the determinations. The deviation of the values of a from electron and x-ray diffraction data makes it possible to visualize the distribution of components in the catalyst and its heterogeneity from the point of view of this distribution. Actually, by electron diffraction relatively thin surface layers of the crystals are studied, whereas by x-ray diffraction the whole volume of the crystals is studied. From the data obtained, it follows that the surface layers of the spinel-phase crystals are richer in Cr_2O_3 than the interior part of the crystals, i.e., that a Cr_2O_3 concentration gradient exists in the spinel-phase crystals: The ratio of components in the surface layers closely

approaches that of a saturated solid solution even for catalysts with low Cr content. The x-ray-determined values of a are "averaged" because of the Cr concentration gradient upon passing into the depth of the crystal. The possibility is not excluded that prolonged thermal treatment at high temperatures might lead to disappearance of the concentration gradient and to formation of homogeneous spinel-phase crystals.

In the catalysts studied, the corundum phase contained both α-Al_2O_3 and α-Cr_2O_3 and apparently their solid solutions, the simultaneous presence of which may be explained by the use of the impregnation method of catalyst preparation.

2. Specific Activity of Catalysts

The specific activity A_{sp} is expressed in the form k/S, where k is the rate constant of the corresponding reaction and S is the value of specific surface of the catalyst. For convenience, all values are shown as 10^6 A_{sp} (in moles/min·m^2). From the results for the basic series A_1-A_9 shown in Fig. 4, it is evident that an increase of Cr_2O_3 and K_2O content causes a rapid decrease of A_{sp} for dehydration and an increase of A_{sp} for dehydrogenation. The variation of A_{sp} for dehydration is regular and continuous. The values of A_{sp} for dehydrogenation show an irregularity for catalyst A_4 and also a decrease for catalyst A_9. A duplicate series of experiments on the decomposition of i-C_3H_7OH with fresh portions of the same A_4 catalyst gave precisely the same results. Therefore, three additional preparations of A_4 were made: two of these samples again gave the same results as those for the basic series of experiments, but the other was somewhat different (A_{sp} somewhat higher). The agreement of results for three out of the four independent preparations

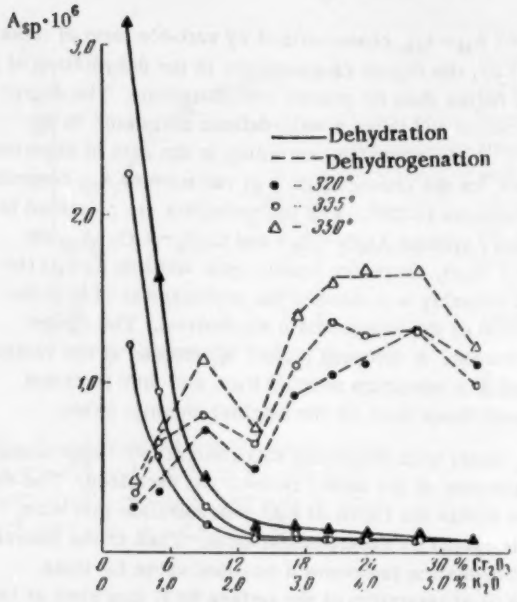


Fig. 4. Variation of specific activity of Al-Cr-K catalysts (A_1-A_9) with composition (vol. rate 2.3 hr^{-1}).

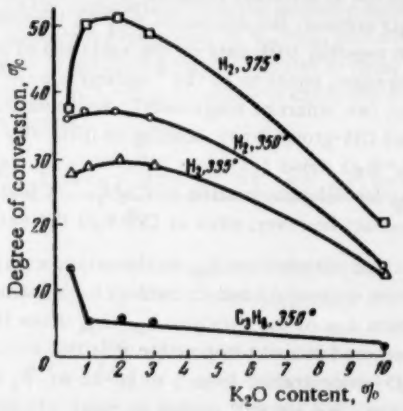


Fig. 5. Influence of K_2O content on activity of Al-Cr-K catalysts. 1) Degree of conversion, %.

of A_4 indicates that the position of the points for A_4 in Fig. 4 (dehydrogenation) is not accidental and is connected with catalyst composition in some still unexplained manner. The decrease of A_{sp} for A_9 (compared to A_8) evidently is connected with the increased quantity of the corundum phase in A_9. Notwithstanding the irregularity of the points for A_4, Fig. 4 shows that the increase of dehydrogenating activity with Cr content is concluded in the region of formation of a saturated solid solution of Cr_2O_3 in γ-Al_2O_3 (at about 20 wt. % Cr_2O_3). With further increase of Cr content (and correspondingly of K) there is little change of activity, but for Cr_2O_3 > 27% the activity decreases. Thus, it is natural to attribute the maximum dehydrogenating activity to the spinel phase of the solid solution. It will be recalled that (as shown above) even with low Cr concentration the surface layers of the crystals of this phase are rather close in composition to that of the saturated solid solution; thus it is also possible to explain their dehydrogenating activity. Up to now the discussion has been concerned with A_{sp} of the catalysts

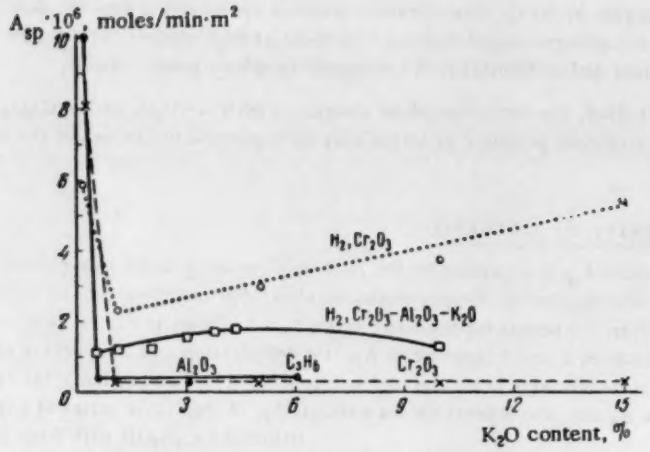


Fig. 6. Influence of addition of K_2O on A_{sp}.

with constant ratio Cr_2O_3: K_2O. Now we turn to the catalysts $A_{10}-A_{14}$, characterized by variable ratio of these components. Figure 5 shows that for all concentrations of K_2O, the degree of conversion in the dehydration of i-C_3H_7OH is low; for 0.5% K_2O the conversion is somewhat higher than for greater concentrations. The degree of conversion in dehydrogenation varies markedly with K_2O content and shows a well-defined maximum in the region of 1-3 wt.% K_2O. The curves of the variation of degree of conversion, according to the data of experiments conducted at different temperatures, are similar. Therefore, for the characteristics of variation of A_{sp} depending on K_2O content, the discussion may be limited to the experiments at 350°. The pertinent data are presented in Fig. 6 together with data on the variation of A_{sp} of the binary systems $Al_2O_3-K_2O$ and $Cr_2O_3-K_2O$. A_{sp} for dehydration, equal to $10 \cdot 10^{-6}$ moles/min·m^2 for the initial Al_2O_3, decreases rapidly upon addition of K_2O (by almost two orders of magnitude). As noted previously, this probably is a result of the replacement of H in the surface OH-groups by K, leading to difficulty in the formation of the intermediate alcoholates. The system $Cr_2O_3-K_2O$ shows analogous behavior with respect to dehydration. A different picture is observed in the variation of A_{sp} for dehydrogenation on Cr_2O_3: at first A_{sp} decreases to a minimum near 1% K_2O, and then increases somewhat; however, even at 15% K_2O the value of A_{sp} is still lower than for the original chromic oxide.

The dehydration A_{sp} of the mixed catalysts $A_{10}-A_{14}$ varies with increasing K_2O content (with approximately constant ratio of Al and Cr oxides) in the same way as in the case of the binary systems just described. The dehydrogenation A_{sp} of the catalysts $A_{10}-A_{14}$ shows little variation within the limits of K_2O concentration that were studied, and it is not impossible that this variation of A_{sp} is caused by experimental error. Then in the interval of K_2O concentration from 1 to 10-15 wt.%, A_{sp} for dehydrogenation represents a constant value for these catalysts. We are still unable to judge whether this is a result of saturation of the surface by K ions even at low K_2O concentrations, or a result of the influence of K_2O on the semiconductor properties of the system. To clarify this question, we are presently studying the electrical properties of $Al_2O_3-Cr_2O_3-K_2O$ catalysts.

3. Selectivity of Catalysts

We evaluated catalyst selectivity on the basis of data for A_{sp} as the fraction of the dehydrogenation reaction in the total of the parallel reactions. Thus, the coefficient of selectivity $K_s = \frac{A_{sp(H_2)}}{A_{sp(H_2)} + A_{sp(C_3H_6)}}$. Values of K_s and its variation with catalyst composition are presented in Fig. 7. The sharp increase of K_s (equal to 0.1 for A_1) at low contents of Cr_2O_3 and K_2O is ended for a catalyst with 18% Cr_2O_3; a further gradual increase of K_s is observed up to 24% Cr_2O_3, and then K_s becomes equal to unity. Thus, with 28% Cr_2O_3 and 5% K_2O in the catalysts, the reaction has shifted almost entirely to dehydrogenation of the alcohol. As clearly seen from the figure, the selectivity coefficients for each of the given catalyst compositions show extremely good agreement. This is manifested in a particularly striking manner by data obtained with catalyst A_4 at temperatures from 320 to 500° and with volume rates from 2.3 to 7 hr^{-1} (based on liquid i-C_3H_7OH). At the same time, the rather

excessive value of K_s at 500° is fully explained by the previously mentioned pyrolysis which occurs at this temperature.

From the experiments conducted with $Cr_2O_3-K_2O$ it follows that the influence of K_2O on K_s is very great. The pertinent data are as follows:

% K_2O	0	1	5	10	15
K_s	0,43	0,96	0,95	0,95	0,95

Thus, the addition of only 1% K_2O leads to a sharp change of selectivity, but further increase of K_2O content does not have any further effect: the surface of the catalyst, from the point of view of selectivity, is already stabilized by the addition of 1% K_2O.

K_s of the mixed catalysts $A_{10}-A_{14}$ varies as follows:

	A_{12}	A_{10}	A_{11}	A_{14}	A_{13}
% K_2O	0,5	1	2	3	10
K_s	0,7	0,86	0,88	0,91	0,95

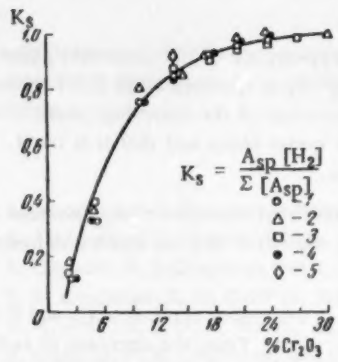


Fig. 7. Catalyst selectivity coefficients: 1) V = 3.5 hr^{-1}, 350°; 2) V = 2.3 hr^{-1}, 320°; 3) V = 2.3 hr^{-1}, 335°; 4) V = 2.3 hr^{-1}, 350°; 5) V = 2.3 hr^{-1}, 500°.

Thus, in the case of the three-component catalyst, only the K_2O content exceeding 3% changes K_s to the same degree as does 1% K_2O added to Cr_2O_3. In the light of what has been said above regarding the phase composition of the catalysts, this may be interpreted thus: stabilization of the surface (with regard to selectivity) apparently becomes possible only after the appearance of excess K_2O (in comparison with the quantity necessary for formation of potassium aluminate) in $A_{10}-A_{14}$ and after it proves possible to form localized regions similar to those formed in the case of $Cr_2O_3-K_2O$ (possibly K-chromite in the form of a surface phase).

4. Activation Energy and k_0 of the Arrhenius Equation

Activation energies were calculated from the values of the reaction rate constants by the Arrhenius equation in the form $E = \frac{\lg k_2 - \lg k_1}{1/T_1 - 1/T_2}$. The data obtained are presented in Table 8. The activation energies for dehydrogenation of $i\text{-}C_3H_7OH$ on catalysts A_2-A_7 are identical and equal to 10 kcal/mole. In comparison with this value, catalyst A_1 (low Cr_2O_3 content) gave a somewhat higher value of E, and catalyst A_8 gave a considerably lower value. The low value for A_8 probably is related directly to the high Cr_2O_3 content, since this value of E (6.4 kcal/mole) coincides with E for dehydrogenation of alcohol on pure Cr_2O_3 [15]. A comparison of the value of E for A_2-A_7 with the just-cited literature data shows that on aluminum–chromium–potassium catalysts the dehydrogenation of alcohol requires a higher activation energy than on pure chromic oxide, i.e., that for this reaction the centers of the aluminum–chromium–potassium catalysts are less active than the centers of chromic oxide catalysts.

The constancy of the value of E for A_2-A_7 evidently has a direct connection with the phase composition of the catalysts and is characteristic of samples containing only one spinel phase. Actually, a saturated solid solution of Cr_2O_3 in γ-Al_2O_3 is formed as the bulk phase in A_6, but in A_2-A_5 it is concentrated (as stated above) in the surface layers of the crystals. In catalyst A_7 that same phase constitutes the base, since it contains only 3% more total Cr_2O_3 than does A_6, but in A_7 the corundum phase is already appearing in small quantity. As seen from Table 8, this shows up not so much in the value of E as in the value of k_0. The constancy of E for A_2-A_7

TABLE 8

Activation Energy for Dehydrogenation and Dehydration of i-C_3H_7OH on $Cr_2O_3-Al_2O_3-K_2O$ Catalysts and Preexponents of the Arrhenius Equation

Catalyst	Dehydrogenation E, kcal/mole	k_0, moles·m^{-2}·min^{-1}	Dehydration E, kcal/mole	k_0, moles·m^{-2}·min^{-1}
A_1	11,5	$2,5\cdot10^7$	23,4	$8\cdot10^{17}$
A_2	10,6	$0,8\cdot10^7$	25,0	$4,4\cdot10^{18}$
A_3	10,0	$1,7\cdot10^7$	20,8	$1,1\cdot10^{17}$
A_4	10,0	$1,2\cdot10^7$	13,4	$4,8\cdot10^8$
A_5	10,0	$1,67\cdot10^7$	9,1	$0,9\cdot10^4$
A_6	10,0	$1,5\cdot10^7$	7,1	$0,13\cdot10^4$
A_7	9,8	$0,3\cdot10^7$	10,0	$0,15\cdot10^4$
A_8	6,4	$0,0002\cdot10^7$	4,5	$0,0003\cdot10^4$

confirms the viewpoint expressed above, that the spinel (γ-) phase of the catalysts studied is more active than the corundum (α-) phase.

An increase of Cr_2O_3 content above 20 wt. % (i.e., after A_6) and the appearance of the corundum phase leads to a sharp decrease of the preexponents k_0, the value of which for A_2-A_7 is approximately constant and averages $1.4\cdot10^7$. The obvious and rather sharp decrease of k_0 upon accumulation of the corundum phase suggests that in the interphase boundaries it blocks the active centers of the spinel phase and that it is itself characterized by greater dispersion of active centers than is the spinel phase.

Passing to the catalysts $A_{10}-A_{14}$ with varying K_2O content, we may state that variation of K_2O content in catalysts with approximately constant ratio Cr_2O_3: Al_2O_3 has little effect on the value of E for alcohol dehydrogenation, which is 10-12 kcal/mole.

The values of E for the dehydration of i-C_3H_7OH decrease rapidly with increasing content of Cr and K in the catalysts. In addition, the values of k_0 also show an extremely sharp decrease. Thus, the decrease of activation energy is compensated by a sharp decrease of the number of active centers of dehydration on the surface as the Cr_2O_3 concentration of the catalysts is increased. The change of the values of E and k_0 for dehydration, which takes place primarily on Al_2O_3, is caused not only by the considerable reduction of Al_2O_3 concentration from catalyst A_1 to catalyst A_9, but also by the accompanying change of its distribution: with increasing Cr_2O_3 content, a smaller and smaller share of the active surface of the spinel phase pertains to dehydration centers (γ-Al_2O_3), and more and more of the low-activity corundum phase is formed.

It was of interest to determine how the addition of K_2O will affect coprecipitated (NH_4OH) aluminum–chromium catalysts. The few experiments which were conducted showed that effects were obtained which were analogous to those described above for impregnated catalysts, down to complete agreement of results. The coprecipitated $Cr_2O_3-Al_2O_3$ catalysts were impregnated with KNO_3 and calcined at 550°, the nitrate being decomposed. The preparation with 15% Cr_2O_3 and 85% Al_2O_3 with the addition of 3% K_2O gave exactly the same results as catalyst A_5 in the decomposition of i-C_3H_7OH.

SUMMARY

1. For the aluminum–chromium–potassium catalysts which were studied, the values of specific surface S pass through a maximum at approximately 10 wt.% Cr_2O_3, the total pore volume decreases from 0.25 cm^3/g at 3-5% Cr_2O_3 to 0.04 cm^3/g at 28-32% Cr_2O_3, and the average pore diameter (40-80 A) passes through a minimum (40 A) near 13% Cr_2O_3. The values of S of the original and used catalysts coincided within the limits of error of the determination.

2. The K-ion in the original and regenerated catalysts is bound in the form OK with Cr^{6+}, and in the used catalysts with Al^{3+}. The phases containing K^+ exist in a dynamic equilibrium, depending on the oxidation-

reduction conditions of the medium. CrOOK was not detected in the original nor in the used catalysts.

3. Catalysts with $Cr_2O_3 \leq 20$ wt.% contain only a phase of the spinel structure, which is a solid solution of Cr_2O_3 in γ-Al_2O_3; this was confirmed by measuring the change of lattice parameter with catalyst composition. The presence of K_2O did not change the concentration limits of the region of existence of this solid solution (compare [7]).

4. The surface layers of the crystals of this solid solution are richer in Cr_2O_3 than the bulk of the crystals, as shown by a comparison of electron and x-ray diffraction data.

5. With content of $Cr_2O_3 > 20$ wt % there appears also a phase of the corundum structure – a solid solution of Al_2O_3 in Cr_2O_3; in the catalytic decomposition of absolute i-C_3H_7OH this phase is considerably less active than the phase with spinel structure.

6. The dehydrogenating specific activity in the decomposition of i-C_3H_7OH passes through a maximum near 20% Cr_2O_3 content in the catalyst, i.e., in the region of saturated solid solution of the spinel structure. The activation energy for i-C_3H_7OH dehydrogenation with 5-23% Cr_2O_3 is equal to 10 kcal/mole. The dehydrating specific activity decreases rapidly with increasing Cr_2O_3 content in the catalyst.

7. A study was made of the influence of the quantity of added K_2O on the catalytic properties of Al_2O_3 and Cr_2O_3; this influence was shown to be stronger than in the case of mixed aluminum–chromium catalysts, where the dehydrogenating specific activity is approximately constant and the dehydrating specific activity is close to zero.

8. Values of selectivity coefficient in the decomposition of i-C_3H_7OH have been determined; it was shown that selectivity depends on composition of the catalysts studied and is little changed over a wide range of process conditions.

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*Original Russian pagination. See C. B. Translation.

THE INFLUENCE OF ACIDITY OF OXIDE CATALYSTS ON THEIR CATALYTIC ACTIVITY

I. POLYMERIZATION OF ISOBUTENE

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The relationship between acidity and catalytic activity was studied on oxide catalysts: $ZrO_2 \cdot SiO_2$, $Al_2O_3 \cdot SiO_2$, $B_2O_3 \cdot Al_2O_3$, $MgO \cdot SiO_2$, and H_3PO_4 on SiO_2. The acidity and number of acid sites were determined by an indicator method. The range of the acidity function H_0 was +4 to −8. The dimerization of isobutene served as a model reaction. The catalytic activity of the samples was determined at a temperature of 150° and partial pressure of isobutene ~380 mm Hg in a circulating-flow unit. It was shown that under these conditions, with a variation of catalyst acidity of five orders of magnitude the dimerization rate changes only fivefold. The order of the dimerization with respect to isobutene on silica−zirconia and aluminosilicate catalysts at a temperature of 150° is equal to 1.6.

A number of processes which are catalyzed by strong acids, for example the dehydration of alcohols, polymerization of olefins, isomerization, etc., also take place on certain solid oxides. B. A. Kazanskii and M. I. Rozengard [1, 2, 3], on the basis of a comparison of the catalytic properties of industrial phosphoric acid and aluminosilicate catalysts, concluded that the reaction mechanisms on these catalysts are identical.

For catalytic reactions taking place in the liquid phase in the presence of protonic acids, a number of investigators have found a linear relationship between the acidity function and the logarithm of the reaction rate constant [4, 5]. A similar relationship was found by Chirkov [6] for a number of processes taking place on films of phosphoric acid and other acids.

It was of considerable interest to determine whether similar regularities also exist for solid oxides possessing acidic properties.

The activity of catalysts having different acidity will depend both on the strength of the acid and on the number of acidic groups per unit surface of the catalyst; therefore, for characterizing the catalyst it is necessary to know both of these values.

The acidic properties of the surface are characterized by the mobility of the hydrogen of the surface hydroxyl groups. This mobility is determined either according to the ability of the hydrogen ion to exchange with another cation or by the ability to ionize an uncharged base. In the first case the acidic properties of the catalyst are characterized by the cation-exchange capacity at the given equilibrium conditions. At present this method is used widely by a number of authors [7, 8, 9, 10].

The reaction of cation exchange may be represented by the equation:

$$AH + K^+ \rightleftarrows AK + H^+,$$

where AH is the acidic group on the surface and K^+ is the exchanging cation in the solution.

Having defined C_{K^+} and C_{H^+} as the equilibrium concentrations of the exchanging cations in the solution, and N_{AK} and N_{AH} as the number of the corresponding cations in the solid phase, the cation-exchange capacity may be written in the following form:

$$N_{AK} = \overline{K} N_{AH} \frac{C_{K^+}}{C_{H^+}},$$

where $\overline{K}$ is the equilibrium constant.

With constant ratio of concentrations of the exchanging cations in the solution, the value of cation-exchange capacity represents the product of the equilibrium constant and the number of acidic groups on the surface. Such an index may be satisfactory in the study of catalysts with different numbers of acidic groups but with identical acidity.

For the study of catalysts with varying acidity, we utilized an indicator method [11, 12, 13]. The method is based on the fact that the indicator (which is a weak base), being adsorbed on a surface possessing acidic properties, is converted to a combined acid; this can be judged by the change of color of the indicator. According to Hammett [13] the acidity function has the following form:

$$H_0 = pK - \lg \frac{C_{BH^+}}{C_B}.$$

Since the indicator color change was observed visually, the magnitude of the second term was not determined. With the presence of ionization of the indicator, it may be said that $H_0 = pK \pm 1$.

A set of eight indicators was available, with pK from +6.8 to −8.2. The characteristics of these indicators are presented in Table 1.

TABLE 1

Name of indicator	Color		pK of transition
	Ionized	Un-ionized	
Neutral red	Red	Yellow	+6.8
Bromcresol purple	Purple	Yellow	+6.1
Bromphenol blue	Yellow	Blue	+3.86
Benzene azodiphenylamine	Purple	Yellow	+1.5
p-Nitrobenzene azo-p-nitrodiphenylamine	Purple	Orange	+0.43
Ditsintalatseton*	Red	Yellow	−3
Benzalacetophenone	Yellow	Colorless	−5.3
Anthraquinone	Yellow	Colorless	−8.2

Since the degree of hydration of the catalyst surface can show a substantial influence both on the catalytic activity and on the results of acidity determinations, the samples studied were previously hydrated under standard conditions.

For this hydration, a sample with grain size 80-100 mesh was treated for one hour at 300° with air saturated with water vapor at room temperature. In view of the small grain size, the hydration was carried out in a fluidized layer. For removal of the physically adsorbed or condensed water (which can alter the results of the acidity determination) the sample after the "steaming" period was evacuated for one hour at 150° and 0.1 mm Hg. The evacuated sample was then transferred in a stream of dry air to dried and weighed test tubes with ground stoppers. After reweighing, the test tubes were filled with dry benzene or heptane, and various quantities of n-butylamine (0.1 N solution in heptane) were added. The contents of the test tubes were mixed for two hours on a magnetic stirrer, after which the suspension was poured into crucibles according to the number of available indicators. To each crucible there was added 3-4 drops of a 0.1% solution of the indicator in benzene, and the color change was observed for the indicator adsorbed on the sample. The maximum acidity of the catalyst was determined without the addition of n-butylamine.

*Transliteration of Russian original.

The objects of investigation were pure and mixed oxides of Groups II, III, and IV of the periodic system, mainly silica – zirconia, silica – magnesia, and alumina – silica catalysts. The chemical composition and characteristics of the samples studied are presented in Table 2.

TABLE 2

Chemical composition of catalysts, wt.%	Method of preparation	Apparent density, g/ml	Surface area, m^2/g	Acidity
Aluminum oxide	Calcination*	0,79	215	+4
Zirconium dioxide	" "	1,1	80	+4
Magnesium hydrosilicate	Coprecipitation	0,56	540	+3,0
42% H_3PO_4 + 58% SiO_2	Impregnation	0,42	—	−5,6
0,8% H_3PO_4 + 99,2% SiO_2	" "	0,41	270	−5,6
2% ZrO_2 + 98% SiO_2	" "	0,42	270	−8,2
10% ZrO_2 + 90% SiO_2	Coprecipitation	0,6	125	−8,2
71% ZrO_2 + 29% SiO_2	" "	0,55	270	−8,2
75% ZrO_2 + 25% SiO_2	" "	0,85	—	−8,2
90% ZrO_2 + 10% SiO_2	" "	0,85	120	−8,2
10% Al_2O_3 + 90% SiO_2	" "	0,7	280	−8,2
0,1% Al_2O_3 + 99,9% SiO_2	Impregnation	0,42	270	−8,2
Titanium dioxide	Through hydroxide	0,72	—	−5,6
Aluminum borate	Impregnation	0,4	—	−5,6
Silica gel	From Na silicate	0,4	—	+4

*Calcination of hydroxide

The results of the study of acidity by the indicator method show that the pure oxides of aluminum, zirconium, and silicon possess weakly acidic properties; they ionize indicators with pK = +4. The mixed oxides ZnO_2 + +SiO_2 and Al_2O_3 + SiO_2 display the properties of strong acids and ionize an indicator with pK = −8.2. This shows that in the process of their preparation an interaction takes place, forming a new complex which possesses the properties of a strong acid. The samples of silica–zirconia catalysts with ZrO_2 content varying from 1 to 90 wt.% have identical maximum acidity, −8.2. Apparently in these cases one and the same compound is obtained, the acidity of which is independent of its concentration in the solid. The same applies to the aluminosilicate samples.

The results are shown in Fig. 1 for the titration of the catalysts by butylamine solution. From the figure it is evident that an increase of the degree of covering of the surface by butylamine molecules causes a decrease of acidity.

As is evident from Fig. 2, the character of the differential curves of acidity distribution depends on the chemical composition of the samples: with content of 2 and 10% ZrO_2 in SiO_2 the bulk of the butylamine is adsorbed within a very narrow interval of acidity; in the case of 71 wt % ZrO_2 (50 mole %) the reduction of acidity takes place more slowly. The acidity of the phosphoric acid catalysts is reduced gradually, which probably is caused by the multibasic character of the phosphoric acid. Upon reducing the acidity to pK = +1 in all cases studied the character of the differential adsorption curves is changed sharply: for the majority of the samples there occurs an increase of adsorption of the base. The sharp change of the course of the adsorption curves apparently denotes a change of the nature of the adsorption. On this basis we have assumed that the number of acidic groups on the surface is determined by the quantity of base adsorbed up to pK = +1.

The influence of the acidity of the oxides on their catalytic activity was studied for the model reaction of isobutene polymerization.

This process was carried out in a circulating-flow unit (Fig. 3). Since the catalyst activity in the reaction studied is dependent on surface water content, the sample was prehydrated as described above. After completion of the hydration and evacuation, nitrogen (deoxygenated on nickel – chromium catalyst) was admitted up to a pressure of 360 mm Hg and the circulating pump was turned on. The temperature was adjusted and isobutene was admitted up to atmospheric pressure, after which the unit was connected to the atmosphere and nitrogen and isobutene were fed in continuously through the gas meters. The gases after passing through the contacting apparatus were cooled in condenser coils, first with tap water and then with ice water. The condensed polymer drained into

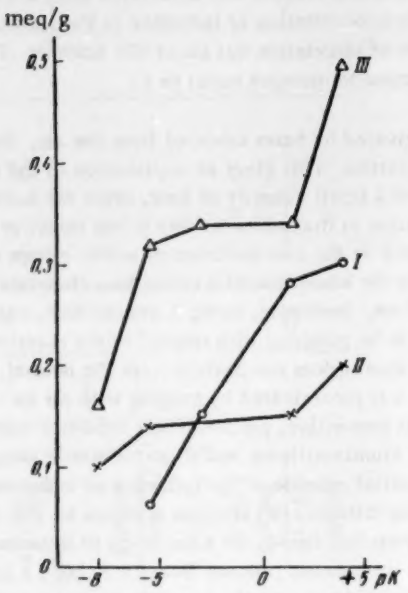

Fig. 1. Effect of adsorption of n-butylamine on catalyst acidity: I) H_3PO_4 on silica gel; II) 2% ZrO_2 + 98% SiO_2; III) 71% ZrO_2 + 29% SiO_2.

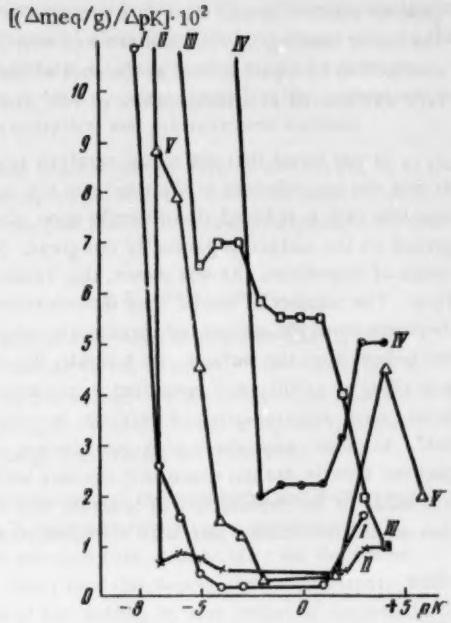

Fig. 2. Differential curve of distribution of concentration of acidic sites according to their acidity: I) 2% ZrO_2 + 98% SiO_2; II) 10% ZrO_2 + 90% SiO_2; III) H_3PO_4 on silica gel; IV) $MgO \cdot SiO_2$; V) 71% ZrO_2 + + 29% SiO_2.

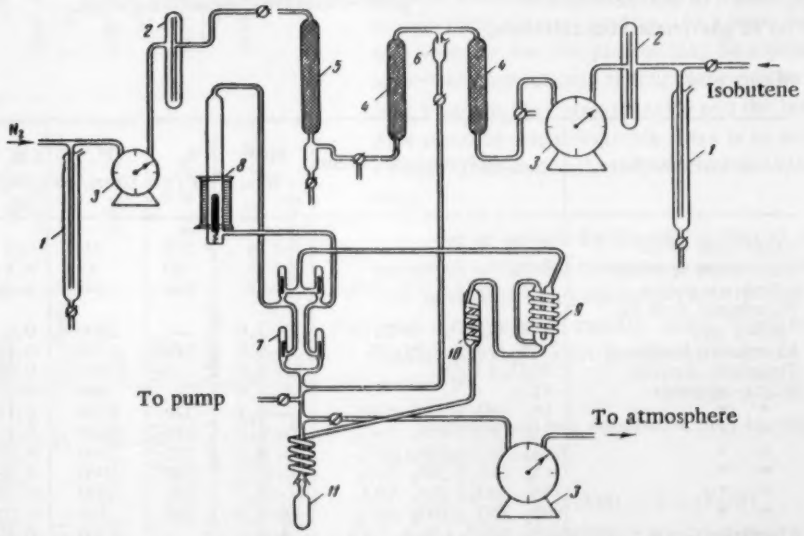

Fig. 3. Diagram of unit for determining catalytic activity of samples: 1) Manostats; 2) rheometers; 3) gas meters; 4) columns with γ-Al_2O_3; 5) deoxygenator; 6) mixer; 7) distribution valve manifold; 8) electromagnetic pump; 9) contacting apparatus; 10) cooler; 11) polymer product receiver.

an ice-cooled receiver. The gases before entering the unit were dried with alumina. Upon leaving the unit, the gaseous mixture passed through a meter The quantity of isobutene reacted was calculated from the difference of the meter readings at the entrance and exit of the unit. The concentration of isobutene in the reaction zone was assumed to be equal to that at the exit of the unit. The rate of circulation was about 800 liters/hr. The reaction rate was studied at a temperature of 150° and ratio of isobutene to nitrogen equal to 1.

It was found that the oxide catalysts are readily deactivated by bases adsorbed from the air. Such poisoning is not always reflected in the results of the acidity determination. This gives an explanation of the fact that the reaction rate is reduced significantly upon adsorption of even a small quantity of base, since the number of acidic groups on the surface is generally not great. The determination of maximum acidity is less sensitive to the presence of impurities. As was shown, this value does not depend on the concentration of acidic groups on the surface. The number of acidic sites is determined according to the adsorption of a strong base (butylamine), which displaces from the surface any previously adsorbed weaker base. Isobutene, being a weaker base, cannot displace the poison from the surface. As a result, the sample proves to be poisoned with respect to the reaction, although according to acidity and according to the number of acidic sites it does not deviate from the normal. Therefore, before each determination of catalytic activity, the sample was preactivated by purging with air for one hour at 500°. In those cases where high-temperature calcination was impossible, precautionary measures were taken so that the sample did not come into contact with air. For the aluminosilicate and silica–zirconia samples, a study was made of the dependence of reaction rate on isobutene partial pressure. The influence of isobutene concentration on polymerization rate with aluminosilicate (I) and silica-zirconia (II) samples is shown in Fig. 4. As is evident from this figure, for a variation of isobutene concentration in the gaseous mixture from 10 to 50%, a linear relationship is observed between the logarithms of rate and concentration. The slope of the line is equal to 1.6. Thus, the dependence of reaction rate on isobutene concentration is expressed by the equation:

$$W = k \cdot C^{1.6}$$

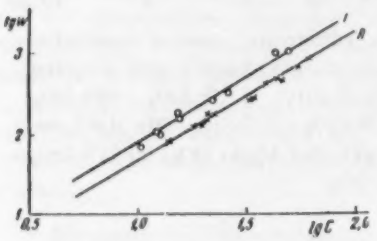

Fig. 4. Dependence of isobutene dimerization rate on its gas-phase concentration.

Results are presented in Table 3 for the study of catalytic activity of the samples. The last column of the table shows values of "specific" activity, i.e., the activity referred to one gram-equivalent of acidic groups.

TABLE 3

Names of samples	Catalyst composition	Max. H_0	S, m^2/g	W, liters/hr·kg	N, equiv/kg	$\frac{W}{N}$
Aluminum oxide	Al_2O_3	+ 4	215	10	0,1	100
Zirconium dioxide	ZrO_2	+ 4	80	4	0,1	40
Silica-magnesia	25% MgO + 75% SiO_2	— 3	540	500	0,26	1900
Phosphoric acid on silica gel	42% H_3PO_4 + 58% SiO_2	—5,6	—	2600	0,6	4300
Aluminum borate	0,8% H_3PO_4 + 99,2% SiO_2	—5,6	270	560	0,16	3800
Titanium dioxide	Al_2O_3 + B_2O_3	—5,6	—	650	0,25	2600
Silica-zirconia	TiO_2	—5,6	—	600	0,25	2400
" "	1% ZrO_2 + 99% SiO_2	—8,2	270	1240	0,14	8900
" "	2% ZrO_2 + 98% SiO_2	—8,2	270	1500	0,15	10000
" "	10% ZrO_2 + 90% SiO_2	—8,2	125	2500	0,27	9300
" "	71% ZrO_2 + 29% SiO_2	—8,2	270	4000	0,38	10500
" "	75% ZrO_2 + 25% SiO_2	—8,2	270	3500	0,33	10600
" "	90% ZrO_2 + 10% SiO_2	—8,2	280	715	0,07	10000
Aluminosilicate	10% Al_2O_3 + 90% SiO_2	—8,2		1500	0,18	8400

TABLE 4

Degree of protonization, $K_p h_0$	Degree of packing, $bp \cdot K_p h_0$	Pressure p	Expression for θ_p $\theta_p = \frac{bp\,K_p\,h_0}{1+bp(1+kh_0)}$	Form of kinetic equation: I $W = k\,\theta_p\,p$	α	n	II $W = k\,\theta_p^2$	α	n	III $W = k\,\theta_p^{\alpha}$	α	n
$\gg 1$	$\gg 1$	High	1	kp	0	1	k	0	0			
$\gg 1$	$\gg 1$	Medium	$\frac{bp\,K_p\,h_0}{1+bp\,K_p\,h_0}$	$\frac{kbp^2\,K_p\,h_0}{1+bp\,K_p\,h_0}$	≤ 1	≤ 2	$\frac{k'b^2p^2h_0^2}{(1+bp\,K_p\,h_0)^2}$	≤ 2	≤ 2			
$\gg 1$	$\ll 1$	Low	$bp\,K_p\,h_0$	$kbp^2\,K_p\,h_0$	1	2	$k'b^2p^2\,K_p\,h_0^2$	2	2			
≤ 1	$bp \gg 1$	High	$K_p\,h_0$	$K'h_0\,p$	1	1	$K'\,h_0^2$	2	2	$k'h_0bp$	1	1
≤ 1	$bp \sim 1$	Medium	$\frac{bp\,K_p\,h_0}{1+bp}$	$\frac{kbp^2\,K_p\,h_0}{1+bp}$	1	≤ 2	$\frac{k'b^2p^2h_0^2}{(1+bp)}$	2	2	$\frac{K'b^2p^2h_0}{(1+bp)^2}$	1	≤ 1
≤ 1	$bp \ll 1$	Low	$bp\,K_p\,h_0$	$kbp^2\,K_p\,h_0$	1	2	$k'b^2p^2h_0^2$	2	2	$K'b^2p^2h_0$	1	2

Note: α-exponent of h_0; n- exponent of p.

The table shows that the catalytic activity of the samples increases with increasing acidity. For the series of silica–zirconia samples having identical maximum acidity the total activity varies by a factor of 5.5; the specific activity, on the contrary, remains constant, depending neither on zirconium dioxide content nor on sample preparation and pretreatment method.

It has been shown by various authors [4, 5, 6] that a relationship exists between catalytic activity of an acid and the function of its acidity, expressed by the equation:

$$\log k + \alpha H_0 = \text{const},$$

where k is the reaction rate constant and H_0 is the acidity function of the catalyst. The coefficient α depends on the nature of the reaction and is equal to 1 or 2. Hence, for a unit change of H_0, the reaction rate should change by a factor of 10 or 100.

Examination of the experimental data presented in Table 3, although revealing a dependence of catalytic reaction rate upon acidity for the system studied, shows that this dependence is different: with variation of the acidity by five orders of magnitude the specific activity increases only fivefold.

Thus, we have found a significantly lesser degree of dependence of reaction rate on catalyst acidity than that described in the literature [4, 5, 6] for processes taking place in solutions.

In order to explain the experimental results obtained, let us examine from a general viewpoint the possible forms of dependence of the rate of a catalytic process upon catalyst acidity. As a basis for reasoning, it is assumed that the process may be represented as an acid–base interchange taking place on the catalyst surface between the catalyst (acid) and the monomer (base). As a result of this interaction there is formed a protonized complex, the conversion of which is the rate-determining step.

Let us assume for simplicity that a) all "acidic" groups on which the catalytic process occurs have identical acidity, b) adsorption equilibrium with the gas phase is established rapidly, and c) equilibrium is also established rapidly for the protonization of the adsorbed molecules.

The latter two conditions may be expressed by the following equations:

$$(KH) + B \rightleftarrows (KHB) \qquad (1)$$

$$(KHB) \rightleftarrows K \ldots HB^{+} \qquad (2)$$

Here (KH) denotes the acid groups on the surface, (KHB) the base (monomer) adsorbed on the acid groups, K...HB^+ the protonized complex, and B the substance [monomer] reacting on the catalyst surface.

Since the reaction rate is a function of the fraction of the surface occupied by protonized molecules, it is advisable to examine the dependence of this value on the acid–base properties of the system and on the conditions of carrying out the reaction.

Let us designate θ_a and θ_p as the fractions of the surface occupied respectively by adsorbed and protonized molecules of the reactant, and θ_0 as the fraction of the active surface which is not occupied by adsorbed molecules.

Since in our experiments the dimer was removed continuously from the reaction zone, the fraction of the surface occupied by dimer molecules may be neglected. Then

$$\theta_a + \theta_p + \theta_0 = 1. \tag{3}$$

The values of θ_a, θ_p, and θ_0 may be expressed by the following equations:

$$\theta_0 = \frac{1}{1 + bp\,(1 + K_p h_0)},$$

$$\theta_a = bp\theta_0,$$

$$\theta_p = \bar{K} h_0 bp\theta_0 = \frac{K_p h_0 bp}{1 + bp\,(1 + K_p h_0)}$$

Here $\underline{p}$ is the partial pressure of the reacting substance, $\bar{K}$ is the equilibrium constant for monomer protonization, h_0 is the acidity of the catalyst, and $\underline{b}$ is the adsorption equilibrium constant.

The reaction rate is proportional to the fraction of the surface occupied by protonized molecules. Upon changing the acid–base properties of the system, θ_p will be changed in the first place owing to the change of the degree of protonization of the adsorbed molecules, since $\theta_p/\theta_a = K_p h_0$.

In the case of strongly acidic catalysts, where almost all of the adsorbed molecules are protonized, θ_p may be changed owing to a change of the degree of surface packing by protonized molecules (θ_p/θ_0), which is equal to $\bar{K} h_0 bp$. Thus, for a given temperature the fraction of the surface packed [occupied] by protonized molecules of monomer depends on the basicity of the reactant, the acidity of the catalyst, and the partial pressure of the reactant.

The form of the kinetic equation depends on the reaction mechanism. For the process in question, the dimerization of isobutene, the following forms of interaction are possible:

1) A protonized molecule may react with a molecule of monomer deposited from the gas phase. In this case the kinetic equation has the form:

$$W = k\theta_p p. \tag{I}$$

2) Two protonized molecules react:

$$W = k\theta_p^2. \tag{II}$$

3) A protonized molecule reacts with an adsorbed but nonprotonized molecule:

$$W = k\theta_p\theta_a. \tag{III}$$

In Table 4 there are presented expressions for θ_p and forms of the kinetic equation in the dimerization reaction of isobutene for catalysts of various acidities, at different pressures.

From the table it is evident that with a high degree of protonization of the adsorbed molecules, when $\bar{K} h_0 \gg 1$, and with high degrees of packing, the reaction rate either is independent of h_0 and $\underline{p}$ or is proportional to pressure to the first power. With high $\bar{K} h_0$ and intermediate degree of packing the exponent of h_0 increases but remains below 2. At very low pressures, where the degree of packing of the surface ($K h_0 bp \ll 1$), a marked relationship

between reaction rate and catalyst acidity is observed. At low degrees of protonization ($Kh_0 \ll 1$) the reaction rate at all pressures should depend on acidity.

In the experimental part of the present study it was shown that for oxide catalysts having acidity functions from −3 to −8 there is very little dependence of reaction rate upon catalyst acidity. This implies that under the conditions of the experiment (150° and 380 mm Hg) almost all of the isobutene adsorbed on the catalyst surface is protonized, even on silica−magnesia catalyst with acidity function equal to −3, and a further increase of acidity naturally cannot change the degree of ionization.

This result differs from that obtained by Chirkov [6] for the same reaction taking place on a film of phosphoric acid. Chirkov found that in the region of acidity from 2 to 4.6 the reaction rate is proportional to the square of the acidity, which is possible only with low degrees of protonization of the dissolved isobutene. Such an essential difference may be explained on the basis that the protonization of adsorbed isobutene proceeds more readily than that of dissolved isobutene.

The authors thank G. K. Boreskov for discussion of the results of the work and for valuable comments.

SUMMARY

1. The acidity and number of acid sites have been determined for a series of oxide catalysts. It was shown that the maximum acidity does not depend on the concentration of acidic component in the catalyst.

2. The dependence of the rate of isobutene dimerization upon catalyst acidity has been determined in the interval of H_0 from −3 to −8. It was found that (at a temperature of 150° and isobutene partial pressure of 380 mm Hg) with a change of acidity of five orders of magnitude the dimerization rate is changed only fivefold. So insignificant a dependence of reaction rate upon acidity indicates that the isobutene adsorbed on the catalyst surface is almost completely protonized.

3. A comparison of the experimental results with literature data on the dimerization of isobutene on films of phosphoric acid permits the conclusion that protonization of adsorbed isobutene proceeds more readily than that of dissolved isobutene.

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THE DETERMINATION OF STABILITY CONDITIONS FOR EXOTHERMIC CONTACT PROCESSES IN A PSEUDOBOILING BED

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In order to ensure stability of the temperature distribution in a contact apparatus with a pseudoboiling bed, it is sufficient, for all practical purposes, that the temperature difference between the catalyst and the cooling agent should be less than a definite critical value. This critical value of the temperature difference depends on the degree of conversion, the temperature, and the kinetic characteristics.

In carrying out many processes involving partial hydrocarbon oxidation, and certain other processes with large heat effects, it is necessary to maintain the temperature within narrow limits in order to obtain high yields of the desired products. By performing such processes in a pseudoboiling bed, of fine grain size, it is possible to prevent overheating of the catalyst surface compared with the gas and to achieve intensive heat transfer to the granule and to the catalyst bed. The yield, from unit volume of contact apparatus with a pseudoboiling bed, is therefore determined by the intensity of heat removal through the cooling surface, with stable stationary conditions. A stable condition is that which arises spontaneously after prevention of disturbances which would cause deviations from the required conditions.

The purpose of this paper is to elucidate the conditions determining the stability limits for exothermic catalytic reactions, occurring in the kinetic region in a pseudoboiling bed with full conversion.

General Equation

Gas, with an initial concentration c_0 of reacting component and at temperature T_1, is admitted to a contact apparatus consisting of a single layer of granular catalyst (Fig. 1).

There is complete mixing of gas and solid particles in the catalyst layer. The concentrations of reactants and products, and the temperature T, are the same for all the particles of the layer. Heat is removed from the contact bed through a cooling surface and by circulation of the catalyst. The temperature of the cooling reagent is T_0, and the initial temperature of the entering catalyst is T_K.

The rate of reaction W (the amount of material reacting in unit time in unit catalyst volume in kg-mole/m^3 · · hr) is determined by the equation

$$W = kf(c), \tag{1}$$

where c is the concentration of reactant in the layer (kg-mole/m^3) and k is the velocity constant, which is a function of temperature T:

$$k = k_0 e^{-\frac{E}{RT}} \tag{2}$$

The total quantity of material reacting in the layer is Wv_K, where v_K is the volume of catalyst in the layer (m^3).

The total amount of reacting material, brought into the apparatus in unit time by the gas stream, is

$$V_g(c_0 - c), \tag{3}$$

where V_g is the rate of gas flow into the apparatus in m^3/hr.

The amount of heat liberated by the reaction is Q_r kcal/hr, where

$$Q_r = W \cdot Q_0 v_k, \tag{4}$$

Q_0 being the heat of reaction in kcal/kg-mole.

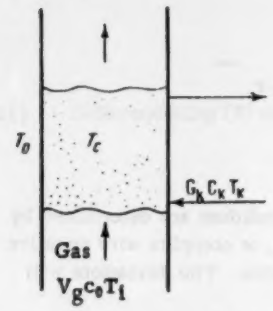

Fig. 1. Diagram of reactor with one layer of catalyst in pseudoboiling state.

The amount of heat removed from the catalyst layer, Q_T in kcal/hr, is given by

$$Q_T = \alpha S(T - T_0) + V_g c_V (T - T_i) + G_K c_K (T - T_K), \tag{5}$$

where α is the heat transfer coefficient in kcal/$m^2 \cdot °C \cdot hr$; S is the cooling surface in m^2; c_V is the specific heat of the reaction mixture in kcal/$m^3 \cdot °C$; G_K is the amount of fresh catalyst added in m^3/hr; T is the temperature of the catalyst layer in °C; c_K is the specific heat of the catalyst in kcal/$m^3 \cdot °C$.

The change in reactant concentration and temperature in the catalyst layer are given by the equations of material and heat balance:

$$v_K \frac{dc}{d\tau} = V_g(c_0 - c) - kf(c) v_K,$$

$$(c_V + c_K) v_K \frac{dT}{d\tau} = kf(c) v_K Q_0 - \alpha S(T - T_0) - V_g c_V (T - T_i) - G_K c_K (T - T_K),$$

or

$$\frac{dc}{d\tau} = \lambda(c_0 - c) - kf(c) = \varphi(c, T) \tag{6}$$

$$\frac{dT}{d\tau} = kf(c)\frac{Q_0}{c_V + c_K} - \frac{\lambda c_V}{c_V + c_K}(T - T_i) - \frac{\alpha S_n}{c_V + c_K}(T - T_0) -$$

$$- \frac{\mu c_K}{c_V + c_K}(T - T_K) = \psi(c, T), \tag{7}$$

where $\lambda = V_g/v_K$ is the space velocity of the gas; $\mu = G_K/v_K$ is the space velocity of the circulating catalyst; S_n is the cooling surface per unit volume of catalyst; τ is the time.

Analysis of the Stability of Stationary States

According to Lyapunov's treatment [1, 2,], changes in deviations of concentration and temperature can be represented by the following differential equations, with a precision down to infinitesimal second order terms:

$$\frac{d}{d\tau}(c - c_s) = \left(\frac{\partial \varphi}{\partial c}\right)_{\substack{c=c_s \\ T=T_s}} (c - c_s) + \left(\frac{\partial \varphi}{\partial T}\right)_{\substack{c=c_s \\ T=T_s}} (T - T_s); \tag{8}$$

$$\frac{d}{d\tau}(T - T_s) = \left(\frac{\partial \psi}{\partial c}\right)_{\substack{c=c_s \\ T=T_s}} (c - c_s) + \left(\frac{\partial \psi}{\partial T}\right)_{\substack{c=c_s \\ T=T_s}} (T - T_s), \tag{9}$$

where c_s and T_s are the concentration and temperature in the stationary state.

The general solutions of these equations are of the form:

$$c - c_s = A_1 e^{\gamma_1 \tau} + A_2 e^{\gamma_2 \tau}, \tag{10}$$

$$T - T_s = B_1 e^{\gamma_1 \tau} + B_2 e^{\gamma_2 \tau}, \tag{11}$$

where γ_1 and γ_2 are the roots of the characteristic Eq. (12) for the system of Eqs. (10)and (11):

$$\gamma^2 - \left[\left(\frac{\partial \varphi}{\partial c}\right)_{c=c_s} + \left(\frac{\partial \psi}{\partial \tau}\right)_{T=T_s}\right]\gamma + \left(\frac{\partial \varphi}{\partial c}\right)_{c=c_s}\left(\frac{\partial \psi}{\partial T}\right)_{T=T_s} - \left(\frac{\partial \psi}{\partial c}\right)_{c=c_s}\left(\frac{\partial \varphi}{\partial T}\right)_{T=T_s} = 0. \tag{12}$$

Only two of the four constants A_1, A_2, B_1, B_2 are independent. The stability conditions are determined by the values of the indices γ_1 and γ_2. If the values of γ_1 and γ_2 are negative and real, or complex with negative real components, then deviations will decrease with time, and the process will be stable. The deviations will increase with time if these conditions are not fulfilled.

The indices will be negative if,

First condition

$$\left(\frac{\partial \varphi}{\partial c}\right)_{c=c_s}\left(\frac{\partial \psi}{\partial T}\right)_{T=T_s} - \left(\frac{\partial \psi}{\partial c}\right)_{c=c_s}\left(\frac{\partial \varphi}{\partial T}\right)_{T=T_s} = l > 0; \tag{13}$$

or, second condition

$$\left(\frac{\partial \varphi}{\partial c}\right)_{c=c_s} + \left(\frac{\partial \psi}{\partial T}\right)_{T=T_s} = m < 0. \tag{14}$$

We find the values of the derivatives to be:

$$\left(\frac{\partial \varphi}{\partial c}\right)_{c=c_s} = -\left(\lambda + k\frac{\partial f(c)}{\partial c}\right) = -\lambda\left\{1 + \frac{kf(c)}{\lambda}\frac{\partial \ln f(c)}{\partial c}\right\} =$$

$$= -\lambda\left\{1 + (c_0 - c)\frac{\partial \ln f(c)}{\partial c}\right\}_{c=c_s}; \tag{15}$$

$$\left(\frac{\partial \varphi}{\partial T}\right)_{T=T_s} = -\left(\frac{kf(c)}{\frac{RT^2}{E}}\right)_{T=T_s}; \tag{16}$$

$$\left(\frac{\partial \psi}{\partial c}\right)_{c=c_s} = k\frac{Q_0}{c_V + c_K}\frac{\partial f(c)}{\partial c} = \frac{kf(c)\,Q_0}{c_V + c_K}\frac{\partial \ln f(c)}{\partial c} = \frac{Q_g}{v_K(c_V + c_K)}\left(\frac{\partial \ln f(c)}{\partial c}\right)_{c=c_s};$$

$$\left(\frac{\partial \psi}{\partial T}\right)_{T=T_s} = \frac{Q_T}{v_K(c_V + c_K)\frac{RT^2}{E}} - \frac{\lambda c_V}{c_V + c_K} - \frac{\alpha S_n}{c_V + c} - \tag{17}$$

$$- \frac{\mu c_K}{c_V + c_K} = \frac{1}{v_K(c_V + c_K)}\left\{\frac{Q_T}{\frac{RT^2}{E}} - \frac{dQ_T}{dT}\right\}_{T=T_s}$$

Substituting the values of the derivatives in Eq. (13) we obtain

$$\frac{Q_r}{v_к(\alpha s_n+\lambda c_V+\mu c_к)}<\frac{RT^2}{E}\left\{1+(c_0-c)\frac{\partial \ln f(c)}{\partial c}\right\}^{*}. \tag{19}$$

We can show that this stability condition implies that, with a change in temperature, the change in the amount of heat evolved must be less than the change in the amount of heat withdrawn from the catalyst layer, i.e.,

$$\frac{dQ_r}{dT}<\frac{dQ_т}{dT}. \tag{19a}$$

Differentiating (4) and (5), and making use of (1) and (2), we obtain

$$\frac{dQ_r}{dT}=Wv_кQ_0\frac{E}{RT^2}+k\frac{df(c)}{dc}\frac{dc}{dT}v_кQ_0 \tag{20}$$

$$\frac{dQ_т}{dT}=\alpha S+V_gc_V+G_кc_к. \tag{21}$$

From Eqs. (3, 4, 5 and 6) we obtain the value of dc/dT in the stationary state, when $Q_r = Q_T$:

$$(c_0-c)V_gQ_0=\alpha S(T-T_0)+V_gc_V(T-T_i)+G_кc_к(T-T_к),$$

$$\frac{dc}{dT}=-\frac{\alpha S+V_gc_V+G_кc_к}{V_gQ_0}. \tag{22}$$

Substituting (20), (21), and (22) in (19), and rearranging, we obtain:

$$Q_r<\frac{RT^2}{E}(\alpha S+V_gc_V+G_кc_к)\left\{1+\frac{Wv_к}{V_g}\frac{\partial \ln f(c)}{\partial c}\right\},$$

and, since $W = \lambda(c_0 - c)$ in the stationary state, we obtain, after substitution, an equation identical with (19):

$$\frac{Q_r}{v_к(\alpha S_n+\lambda c_V+\mu c_к)}<\left\{1+(c_0-c)\frac{\partial \ln f(c)}{\partial c}\right\}\frac{RT^2}{E}.$$

In the stationary state $Q_r = Q_T$ and

$$Q_r=\alpha S_n(T-T_0)+\lambda c_V(T-T_i)+\mu c_к(T-T_к). \tag{23}$$

Substituting (23) in (18), we obtain:

$$\frac{\alpha S_n(T-T_0)+\lambda c_V(T-T_i)+\mu c_к(T-T_к)}{(\alpha S_n+\lambda c_V+\mu c_к)\frac{RT^2}{E}}<1+(c_0-c)\frac{\partial \ln f(c)}{\partial c}. \tag{24}$$

If the heat is completely removed only through the walls, then

$$\frac{T-T_0}{\frac{RT^2}{E}}<1+(c_0-c)\frac{\partial \ln f(c)}{\partial c}. \tag{25}$$

*For simplicity, the indices of the stationary state are not shown in the formulae.

If the heat is only removed by catalyst circulation, then

$$\frac{T-T_к}{\frac{RT^2}{E}} < 1 + (c_0 - c)\frac{\partial \ln f(c)}{\partial c}. \tag{26}$$

Correspondingly, for an adiabatic process without catalyst circulation ($S_п = 0$, $\mu = 0$):

$$\frac{T-T_1}{\frac{RT^2}{E}} < 1 + (c_0 - c)\frac{\partial \ln f(c)}{\partial c}. \tag{27}$$

Equations (25, 26), and (27) show that the value of

$$1 + (c_0 - c)\frac{\partial \ln f(c)}{\partial c}$$

determines the maximum value of the temperature difference for all forms of heat removal and is the restricting criterion. Let it be denoted by Pm (the temperature difference criterion).

This criterion depends only on the degree of conversion, the mathematical form of the relation between reaction velocity and reactant concentrations, the temperature, and the activation energy.

If all methods of heat removal are used simultaneously, and if the initial temperatures of the gas and circulating catalyst are equal to the temperature of the cooling reagent, then, according to the inequality (24), the temperature difference should be less than the criterion Pm. In the general case, using the heat balance Eq. (23), the inequality (18) can be put in the form:

$$\frac{T-T_0}{\frac{RT^2}{E}} < Pm - U, \tag{28}$$

where

$$U = \frac{\lambda c_V (T_0 - T_1) + \mu c_к (T_0 - T_к)}{(\alpha S_п + \lambda c_V + \mu c_к)\frac{RT^2}{E}}. \tag{29}$$

It follows from (28) and (29) that, if the initial temperatures of the gas and circulating catalyst are less than the temperature of the cooling reagent, then the permissible difference in temperature between the catalyst layer and the cooling reagent should decrease in accordance with the heat balance equation. This indicates that it is impossible, by changing the initial temperature of the gas or circulating catalyst, to alter the necessary size of the cooling surface, which, according to the inequality (18), depends only on the value of the temperature difference criterion, the heat transfer coefficient, and the space velocities of the gas and circulating catalyst.

After substituting the values of the differentials in the inequality (14), corresponding to the second condition, we obtain:

$$-\lambda\left\{1 + (c_0 - c)\frac{\partial \ln f(c)}{\partial c}\right\} + \frac{1}{v_к (c_V + c_к)}\left\{\frac{Q_T}{\frac{RT^2}{E}} - \frac{dQ_T}{dT}\right\} < 0. \tag{30}$$

Hence,

$$\frac{dQ_T}{dT} > \frac{Q_r}{\frac{RT^2}{E}} - \lambda (c_v + c_k) v_k P m. \tag{31}$$

In order to understand the physical significance of the second condition, let us consider the case when the first condition (13) is fulfilled and the second (14), is not. This implies that $l > 0$ and $m > 0$.

Let Eq. (12) be rewritten in the form:

$$\gamma^2 - m\gamma + l = 0,$$

so that $\gamma_{1,2} = \frac{m \pm \sqrt{m^2 - 4l}}{2}$.

If $m^2 - 4l < 0$, then the roots of the equation are complex. The general solution of the system of equations will have the form:

$$c - c_s = Ae^{\frac{m}{2}} \sin(\omega\tau + \varphi_1),$$

$$T - T_s = Be^{\frac{m}{2}} \sin(\omega\tau + \varphi_2),$$

where $\omega = \frac{\sqrt{4l^2 - m^2}}{2}$, A, B, φ_1, φ_2 are constants, of which only two are independent.

If $m > 0$, the variations in temperature and concentration in the reactor will increase with time – the state will be unstable. If $m < 0$, the variations will die out with time – the condition will be stable.

Thus, in the general case, the stability condition [3] $dQ_T/dT > dQ_r/dT$ is necessary but not sufficient. Increasing variations in concentration and temperature can arise if the first condition is fulfilled. However, increasing variations do not occur with processes taking place in a pseudoboiling bed, because of the high thermal capacity of unit volume of catalyst. The value of the second term of the inequality (30):

$$\frac{1}{v_k (c_v + c_k)} \left(\frac{Q_r}{\frac{RT^2}{E}} - \frac{dQ_T}{dT} \right)$$

is less than the absolute value of the first term $-\lambda Pm$ – and the inequality (30) is achieved for all practical cases ($m < 0$). Thus, in order that the catalytic process in the pseudoboiling bed should be stable, it is necessary and sufficient that only the first condition should be fulfilled – inequality (28).

As an example, we shall find the minimum value of the cooling surface for unit catalyst volume to ensure stable conditions for ethylene oxidation to ethylene oxide in a pseudoboiling bed.

The conditions are: temperature 230°; gas space velocity 9250 hr^{-1}; heat is removed only through the cooling surface wall; the heat transfer coefficient is 200 kcal/$m^2 \cdot hr \cdot °C$; the selectivity is 0.65; the heat effect for 0.65 selectivity is 140,000 kcal/kg-mole; the initial ethylene concentration is 1.52×10^{-3} kg-mole/m^3; the activation energy is 17,500 kcal/kg-mole; the cooling agent temperature and the initial gas temperature are equal; the initial degree of conversion is zero; the final degree of conversion is 0.3; the rate of reaction for the initial stage of the oxidation process can be expressed by a first order equation $f(c) = c$; the specific heat of the catalyst $c_K = 300$ kcal/$m^3 \cdot °C$; the specific heat of the gaseous reaction mixture is 0.32 kcal/$m^3 \cdot °C$.

The inequality (19) is used to find the minimum value of the surface for unit catalyst volume ($v_K = 1$), when $\mu = 0$:

$$S_n > \frac{\frac{Q_r}{\frac{RT^2}{E}\left\{1 + (c_0 - c)\frac{\partial \ln f(c)}{\partial c}\right\}} - \lambda c_v}{\alpha}$$

$$Q_r = \lambda c_0 (x - x_i) Q_0 = 9250 \cdot 1{,}52 \cdot 10^{-3} \cdot 0{,}3 \cdot 140\,000 = 590\,000 \text{ cal/hr};$$

$$\lambda c_v = 9250 \cdot 0{,}32 = 2960 \text{ cal/m}^3 \cdot ^\circ\text{C} \cdot \text{hr};$$

$$\frac{RT^2}{E} = \frac{2 \cdot 503^2}{17\,500} = 28{,}9,$$

$$1 + (c_0 - c)\frac{\partial \ln f(c)}{\partial c} = \frac{c_0}{c} = \frac{c_0}{0{,}7\,c_0} = 1{,}43.$$

Substituting, we obtain:

$$s_n > \frac{\frac{590\,000}{28{,}9 \cdot 1{,}43} - 2960}{200} = 57 \quad \text{m}^2/\text{m}^3.$$

The inequality (30) is used as a check:

$$\frac{dQ_r}{dT} = \alpha s_n + \lambda c_v = 200 \cdot 57 + 2960 = 14\,300 \quad \text{cal/m}^3 \cdot ^\circ\text{C} \cdot \text{hr},$$

$$-9250 \cdot 1{,}43 + \frac{1}{(0{,}32 + 300)}\left(\frac{590\,000}{28{,}9} - 14\,300\right) = -13\,200 + 20{,}3 = -13\,180.$$

Calculation of the Temperature Difference Criterion

The values of the temperature difference criterion, as a function of the degree of conversion, have been determined for reactions of the first and n-th order, and for two cases of retardation by products. If no account is taken of the change in volume of the gas mixture during the reaction, then the initial degree of conversion of reactants, before the catalyst layer, is determined from the concentration (c_i) at the start of the given layer, corresponding to $x_i = 1 - (c_i/c_0)$. The degree of conversion in the layer is $x = 1 - (c/c_0)$.

The calculated results for the values of the criteria are shown in Tables 1 and 2.

Table 1 gives the mathematical relations between temperature difference criterion and degree of conversion, while Table 2 gives the calculated values Pm.

Adiabatic Process. For an adiabatic process, the temperature will increase continuously with increasing degree of conversion. The rise in the temperature is given by the equation:

$$T - T_i = \Delta T_m (x - x_i), \tag{32}$$

where ΔT_m is the temperature rise in °C when the adiabatic process proceeds to completion. According to inequality (27), for an adiabatic process, the temperature difference between catalyst layer and initial gas temperature should be less than the temperature difference criterion:

$$\frac{T - T_i}{\frac{RT^2}{E}} < Pm.$$

TABLE 1

The Dependence of the Temperature Difference Criterion Pm on the Degree of Conversion for Different Types of Reaction

Reaction Type	Form of function f(c)	Criterion Pm.
Zero order reaction	Does not vary	1
First order reaction	c	$1+\frac{x-x_i}{1-x}$
n-th order reaction	c^n	$1+\frac{n(x-x_i)}{1-x}$
Reactions retarded by products	$\frac{c}{\sqrt{c_0-c}}$	$1+\frac{(x-x_i)(1+x)}{2(1-x)\cdot x}$
	$\frac{c}{c_0-c}$	$1+\frac{x-x_i}{(1-x)x}$

TABLE 2

Values of the Temperature Difference Criterion Pm as a Function of the Degree of Conversion for Different Reactions at $x_i = 0$

Degree of conversion.	Zero order f(c)=const.	First order, f(c)=c	n-th order, $f(c)=c^n$	Reactions retarded by products	
				$f(c)=\frac{c}{\sqrt{c_0-c}}$	$f(c)=\frac{c}{c_0-c}$
0,3	1	1,43	$1+0,43\,n$	1,93	2,45
0,5	1	2,00	$1+n$	2,50	3,00
0,6	1	2,50	$1+1,5\,n$	3,00	3,50
0,7	1	3,34	$1+2,34\,n$	3,84	4,34
0,8	1	5,00	$1+4\,n$	5,50	6,00
0,85	1	6,67	$1+5,57\,n$	6,50	7,00
0,9	1	10,0	$1+9\,n$	10,5	11,0
0,95	1	20,0	$1+19\,n$	20,5	21,0

According to Eq. (32) and inequality (27), for an adiabatic process, the increment in the degree of conversion in the catalyst layer should be less than a certain value:

$$x - x_i < \frac{Pm\frac{RT^2}{E}}{\Delta T_m}. \tag{33}$$

If we substitute in the inequality (33) the temperature difference criteria expressed in terms of the degree of conversion in accordance with Table 1, then we obtain a series of inequalities to determine the maximum achievable degrees of conversion in a single pseudoboiling catalyst layer, with complete mixing of gas and solid particles:

for a zero order reaction

$$x - x_i < \frac{1}{\Delta\theta_m}; \tag{34}$$

for a first order reaction

$$\frac{1}{x - x_i} + \frac{1}{1 - x} > \Delta\theta_m; \tag{35}$$

for an n-th order reaction

$$\frac{1}{x - x_i} + \frac{n}{1 - x} > \Delta\theta_m; \tag{36}$$

for reactions with retardation by-products

$$f(c) = \frac{c}{\sqrt{c_0 - c}}; \quad \frac{1}{x - x_i} + \frac{1 - x}{2(1 - x)x} > \Delta\theta_m, \tag{37}$$

$$f(c) = \frac{c}{c_0 - c}; \quad \frac{1}{x - x_i} + \frac{1}{(1 - x)x} > \Delta\theta_m. \tag{38}$$

where $\Delta\theta_m = \frac{\Delta T_m E}{RT^2}$ is the temperature rise of the gas mixture, in dimensionless units, for an adiabatic process proceeding to complete conversion.

As an example, we will calculate the maximum degrees of conversion in a single layer for the adiabatic oxidation of ethylene to ethylene oxide [4]. Graphs (Fig. 2) are constructed for this purpose for the left-hand side of the inequality (38), when $f(c) = \frac{c}{c_0 - c}$ i.e., $\psi(x) = \frac{1}{x - x_i} + \frac{1}{(1 - x)x}$ for different initial degrees of conversion.

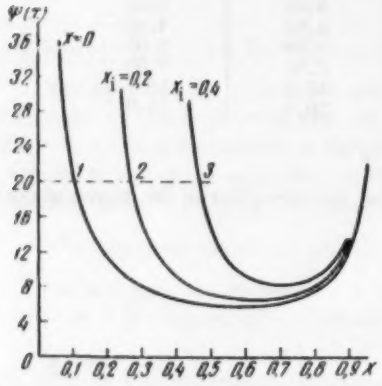

Fig. 2. Graphs of the function $\psi(x) = \frac{1}{x - x_i} + \frac{1}{(1-x)x}$

The adiabatic temperature rise for complete conversion of a 3% ethylene in air mixture, with a selectivity of 0.65, is 580°. With a catalyst temperature of 230°, the adiabatic temperature rise in dimensionless form is 20.

A line is now drawn parallel to the x-axis for $\Delta\theta_m = 20$. The points of intersection 1, 2, and 3 give the maximum possible degree of conversion in a single layer for the adiabatic reaction: for $x_i = 0$, $x_{max} = 0.11$; for $x_i = 0.2$, $x_{max} = 0.27$; for $x_i = 0.4$, $x_{max} = 0.467$.

The author wishes to thank G. K. Boreskov for discussing the results of the work.

SUMMARY

1. To ensure stable temperature conditions in a contact apparatus, with pseudoboiling bed and heat removal through a cooling surface, it is sufficient, for all practical purposes, that the temperature difference between the catalyst and the cooling agent should be less than a definite critical value:

$$T - T_0 < \frac{RT^2}{E}(Pm - U).$$

2. This critical condition is also valid for other means of removing the heat of reaction – circulation of catalyst or reaction mixture. In this case, there is a limiting temperature difference between the bed temperature and the initial temperature of the circulating catalyst or reaction mixture.

3. The value of this critical temperature difference depends on the degree of conversion, the temperature, and the kinetic characteristics of the reaction.

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PRINCIPLES OF REACTOR OPERATION CONTROL IN LARGE-TONNAGE CATALYTIC PROCESSES*

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This article is devoted to the problem of developing efficient types of industrial reactors for large-tonnage catalytic processes. The article includes an examination of technological methods of controlling reaction rate in industrial reactor installations, means of intensifying their operation, methods of evaluating reactor operation, and also questions of classification and technological principles of reactor construction.

In the present article attention is given to methods of regulating reaction rate in industrial chemical reactors, means of intensifying their operation, methods of evaluating their operation, and technological principles for the construction of high-output contacting apparatus.** Here the most general and important problems are taken up; these constitute only a part of the theory of industrial chemical reactors.

The condition of ideal displacement, in which longitudinal diffusion and mixing of the initial and final materials are entirely absent, can be realized only in relatively low-capacity reactors with high length-diameter ratio, for example the pipe-coil or tubular type. The practical achievement of chemical conversions in high-capacity industrial reactors often is accompanied by the establishment of some circulation within the reactor, leading to mixing of the raw material and the reaction products. Together with diffusion complications and the instability of temperature at individual points of the reactor, intrareactor mixing may be a significant factor in the deviation of the macrokinetics of industrial processes from the corresponding laboratory data.

The relative intensity of internal mixing r may be defined as the ratio of the weight of recirculating product stream G_c to the weight of unconverted raw material G_u [2, 3, 4]:

$$r = G_c : G_u. \tag{1}$$

Equation (2) defines the initial depth of conversion of the mixed stream y_r, increasing with an increase of the relative intensity of mixing or with an increase of the difference in the depth of conversion of the mixing streams: of the reaction products y_p and of the fresh raw material [feed] y_f:

$$y_r = y_p - \frac{y_p - y_f}{1 + r}. \tag{2}$$

*Presented at the All-Union Conference on Organic Catalysis, November 20, 1959.

**A more detailed discussion of these questions was given by the authors together with A. N. Planovskii in a paper at the Fifth International Petroleum Congress [1].

In the limiting case of ideal displacement, the depth of conversion of the mixed raw material is equal to the initial depth of conversion of the fresh raw material:

$$\lim_{r \to 0} y_r = y_f \tag{3}$$

For ideal [complete] mixing, y_r is equal to the final depth of conversion of the fresh raw material

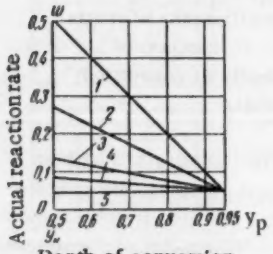
$$\lim_{r \to \infty} y_r = y_p. \tag{4}$$

The change of the actual initial reaction rate w_r of the mixed raw material with varying mixing intensity r can be shown in the case of an irreversible first-order reaction without change in the number of moles (A → R) as follows:

$$w_r = k_1 a \left(1 - y_p + \frac{y_p - y_f}{1 + r}\right); \tag{5}$$

$$\lim_{r \to 0} w_r = k_1 a (1 - y_f) = w_f; \tag{6}$$

$$\lim_{r \to \infty} w_r = k_1 a (1 - y_p) = w_p \tag{7}$$



Depth of conversion of fresh raw material

Fig. 1. Change of actual rate of reaction (A → R) in flow-type reactors with varying relative intensity of mixing r at constant total depth of conversion of fresh raw material (y_p): 1) r = 0; 2) r = 1; 3) r = 4; 4) r = 9; 5) r = ∞.

From these equations and Fig. 1 it is evident that the greatest reaction rate occurs under conditions of ideal displacement. As the relative intensity of mixing is increased, the reaction rate decreases; under conditions of ideal [complete] mixing, the reaction rate remains constant and equal to the rate at final depth of conversion w_p (4).

The change of operating concentrations and weight of material streams which is brought about by the mixing of raw material with conversion products is reflected in the average rate of chemical conversion w_{av} and consequently in the volume of the reactor. It has been proposed to apply the name "concentration efficiency" [2, 3, 5] to the ratio of the volume of a standard reactor with ideal displacement ($V_{r_{std}}$) to the volume of apparatus with mixing (V_r); this is defined by the equation

$$\eta_c = w_{av} : w_{av_{std}} = V_{r_{std}} : V_r; \tag{8}$$

the inverse of this value is then the relative volume of the reactor in terms of concentration

$$Y_c = V_r : V_{r_{std}}. \tag{9}$$

Both of these ratios are dimensionless and do not depend on the value of the rate constant of the reaction. It is assumed that the temperature conditions in the two reactors are identical.

In Fig. 2 there are presented curves of concentration efficiency for an irreversible first-order reaction which is retarded by the products of conversion (with an increase of the number of moles, A → νR) [3]. From this figure it can be seen that the influence of intrareactor circulation is especially great when it first arises, in the interval of relative intensity r from 0 to 1. When moderate mixing intensity has been established (in the order of 8 to 10), the values of concentration efficiency are close to the efficiency for complete mixing. In the range of greater depths of conversion the concentration efficiencies are reduced sharply.

The curves of concentration efficiency have a two-fold application. On the one hand, it is easy with their help to determine the reactor volumes necessary for a given depth of conversion with various intensities of mixing; on the other hand, the curves graphically illustrate the change of depth of conversion (in a reactor with a given volume) as a different ratio of internal circulation is established.

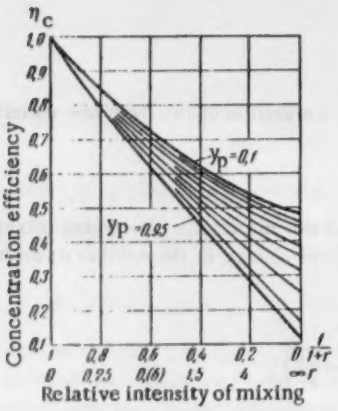


Fig. 2. Concentration efficiencies of flow-type reactors with various intensities of mixing and final depths of conversion (y_p) for an irreversible first-order reaction, retarded by the conversion products.

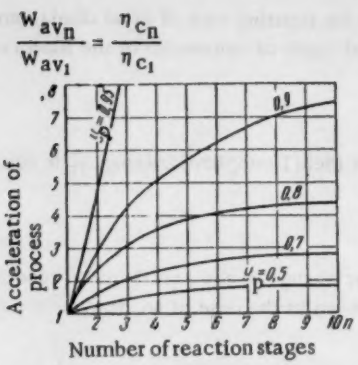


Fig. 3. Acceleration of a second-order process by series sectionalization (n) of flow-type reactors, in comparison with single-stage reaction. w_{av_n}, η_{c_n}) average reaction rate and concentration efficiency for sectionalized reactor; w_{av_1}, η_{c_1}) average rate and concentration efficiency of single-stage reactor; $y_f = 0$; numbers of curves are final depths of conversion of fresh raw material.

Since the influence of intrareactor circulation increases with an increase of its intensity and with an increase of the difference between the depths of conversion of the mixing streams, two methods are possible for regulating the working concentrations in reactors where mixing is encountered: the first is decreasing the intensity of intrareactor mixing, and the second is decreasing the concentration differential of the streams being mixed. Both of these methods can be accomplished by separating the reaction zone into a number of sections. In the first method the reacting stream passes through a number of parallel sections with high ratio of length to diameter. The same final depth of conversion is attained in each of the sections. In the second method the reacting mixture passes successively through a number of sections, in each of which there occurs only a partial, stepwise increase of conversion depth.

Curves are shown in Fig. 3 for the acceleration of a second-order reaction by series sectionalization of the reaction zone. From these curves it may be seen that at moderate over-all depths of conversion the greatest effect is given by the introduction of the first three to four successive stages. If it is necessary to attain high degrees of final conversion, the effective number of successive sections is increased.

Series sectionalization facilitates multizone feed of the most reactive component.

For multiphase systems this method permits multistage countercurrent contacting of the heterogeneous components.

Economical sizes of reactor installations are ensured by regulating not only the working concentrations, but also the temperature conditions in the apparatus, which also influence the rate and course of the chemical conversion.

The basic principles of the theory of thermal regulation of chemical conversion rate still have not been generalized in the broad scientific-technical press, in spite of their great importance in controlling the operation of industrial reactors.

Any lowering of temperature (as compared to the optimum) effects a reduction of the reaction rate and consequently an increase in the expense of reactor volume. For conversions that are highly complex and reversible, deviation from the optimum conditions may be accompanied by a change of the reaction course as well as its rate.

By a method analogous to that used to evaluate the effect of working concentrations on reaction rate, the influence of reactor temperature conditions may be expressed by the ratio of the average rates or volumes of a nonisothermal reactor V_r to those of a standard reactor with optimum conditions $V_{r_{std}}$. It is proposed to call the ratio

$$\eta_t = w_{av} : w_{av_{std}} = V_{r_{std}} : V_r \qquad (10)$$

the temperature efficiency of the reactor with nonisothermal temperature conditions. The reciprocal of the temperature efficiency is called the relative reactor volume according to temperature [6, 7, 8]

$$Y_t = V_r : V_{r_{std}}. \qquad (11)$$

Both of these ratios are dimensionless and are independent of the value of the reaction rate constant.

A large range in the longitudinal temperature distribution of a flow-type reactor makes it difficult to evaluate the advantages or disadvantages of various temperature conditions in the reaction zone.

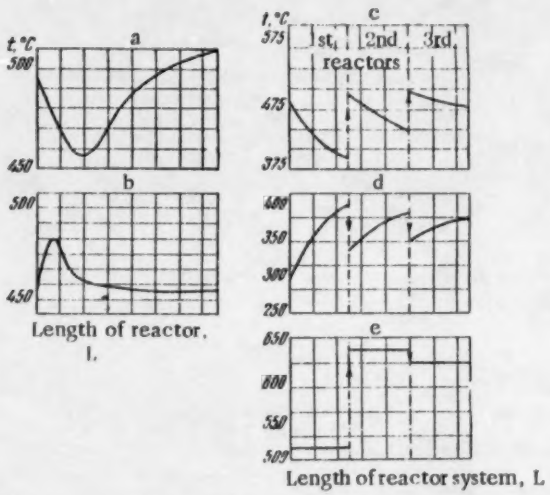


Fig. 4. Longitudinal temperature distribution of reactors with continuous or stepwise heat exchange: a) Ultraforming reactor with continuous heat exchange, b) hydrocarbon synthesis reactor with continuous heat exchange, c) three-reactor ultraforming block with stepwise heat exchange, d) three-reactor gasoline hydropurification block with stepwise heat exchange, e) stepwise countercurrent regenerator with fluidized bed of cracking catalyst.

The curves in Fig. 4 show the temperature distribution along the reacting stream in single- and multi-reactor systems with continuous or stepwise heat exchange [1, 9]. A direct comparison of these systems is possible only in cases where the temperature curves of the nonisothermal reactor can be expressed by a single characteristic temperature. Since the depth of conversion attained in such a reactor is determined by the average rate at which the reaction proceeds, the single characteristic value which must be taken is the temperature which is equivalent to this average rate. This may also be called the equivalent isothermal temperature.

This temperature depends on the activation energy or temperature coefficient of reaction rate, the range of temperature variation, and the nature of temperature distribution in the reaction zone.

In determining equivalent isothermal temperature, the simplest case is for constant linear increase or decrease of t along the reactor. The expression for equivalent isothermal temperature as a function of activation energy is complex and hence difficult to use [9]. The equivalent isothermal temperature is defined more simply in relation to the temperature coefficient of reaction rate (k_t); in a reactor with linear temperature variation from the lower temperature t_1 to the higher temperature t_2 this relationship is given by [6, 7, 8]

$$t_{es} = t_1 + \frac{10}{\ln k_t} \ln \frac{k_t^{0.1(t_2 - t_1)} - 1}{0.1 (t_2 - t_1) \ln k_t} \qquad (12)$$

For any other temperature curve (nonlinear) it is necessary to use an approximate method, breaking the curve into segments and determining the individual equivalent isothermal temperatures for the separate linear segments by the preceding formula. These individual temperatures are then combined into an over-all temperature t_{ei} for the curve, equivalent to the average reaction rate, by means of the following equation [9]:

$$t_{ei} = t_1 + \frac{10}{\ln k_t} \ln \left[\sum_i z_i k_t^{0.1 (t_{es_i} - t_1)} \right] \qquad (13)$$

The value of equivalent isothermal temperature makes it possible to evaluate the influence of temperature distribution (along the reacting stream) upon the reaction rate and volume of the apparatus.

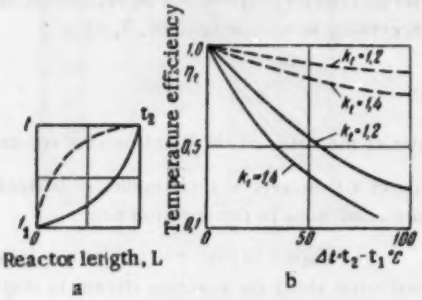


Fig. 5. Temperature efficiencies of flow-type nonisothermal reactors (ideal displacement) with different temperature distributions in the reaction zone: a) Temperature distribution in the reaction zone; b) temperature efficiency; t_1 = lower temperature, t_2 = higher temperature.

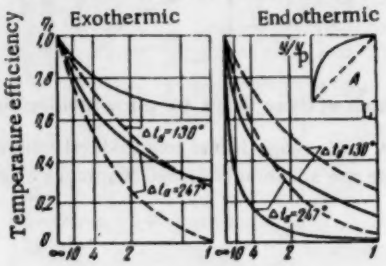


Fig. 6. Temperature efficiencies of flow-type reactors (ideal displacement) with stepwise heat exchange for exo- and endothermic processes with different kinetic curves: A) Kinetic curve y vs. L at t = constant.

Temperature efficiencies are reduced by an increase of the difference between the standard optimum temperature t_{std} and the equivalent isothermal temperature, and also by an increase of the temperature coefficient of reaction rate:

$$\eta_t = k_t^{-0.1 (t_{std} - t_{ei})} \qquad (14)$$

From Fig. 5 it can be seen that the lowest temperature efficiencies and consequently the largest reactor volumes are obtained with temperature curves that are concave in relation to the reactor longitudinal axis; on the other hand, the highest efficiencies are obtained with convex temperature curves [1, 3].

In Fig. 6 temperature efficiencies are shown for reactors consisting of a series of adiabatic stages with intermediate heat exchange; efficiency plots are shown for chemical conversions with different kinetic curves [1, 3]. It can be seen that for either exothermic or endothermic conversions the temperature efficiencies decrease with an increase of the temperature change observed under purely adiabatic conditions Δt_a; the temperature efficiencies increase with an increase of the number of heat-regulating stages n.

The character of the kinetic curve has a different influence on the temperature efficiencies of reactors for chemical conversions with opposite heating effects. A large deviation of the reaction rate–time relationship (convex kinetic curve) brings an increase of temperature efficiencies for exothermic processes and, on the contrary, a decrease of temperature efficiencies for endothermic processes.

The dual reduction of rate caused by lowering concentration and temperature of the reacting stream makes it particularly disadvantageous to apply purely adiabatic reactors for attaining deep conversion in highly endothermic reactions. The greatest effect is given by the introduction of the first few successive stages of temperature regulation. The greater the total temperature change under adiabatic conditions, the greater the number of stages required to attain the same intensity of the reaction course. Stepwise temperature regulation is especially effective in intensifying the course of highly endothermic conversions which have large rate deviation and high activation energy.

Mixing the raw material with the conversion products and the resulting heat exchange between them reduces the temperature change in the reactor Δt_r in comparison with the temperature change under adiabatic conditions Δt_a:

$$t_r = \frac{\Delta t_a}{1 + r}. \qquad (15)$$

Because of this, the industrial accomplishment of rapid, temperature-sensitive, highly exothermic conversions is aided substantially by the use of reactors with internal or external circulation of reaction products.

A combination of stepwise regulation of temperature conditions (increasing temperature efficiencies of the reactors) and stepwise regulation of working concentrations (given high concentration efficiencies) ensures high intensity of the course of many chemical conversions under industrial conditions.

The product of concentration and temperature efficiencies will characterize the over-all efficiency of operation of industrial nonisothermal reactors with internal mixing, in comparison with an isothermal reactor with ideal displacement.

The methods of regulating reaction rate established the technological principles of determining the structural shape of reactor installations. It is advisable to examine from these viewpoints the generalized classification of the basic technological designs for flow-type reactors in the instance of multicomponent systems with pseudoliquefied [fluidized] powdered catalyst, which are very likely candidates in creating plant systems of high productivity.

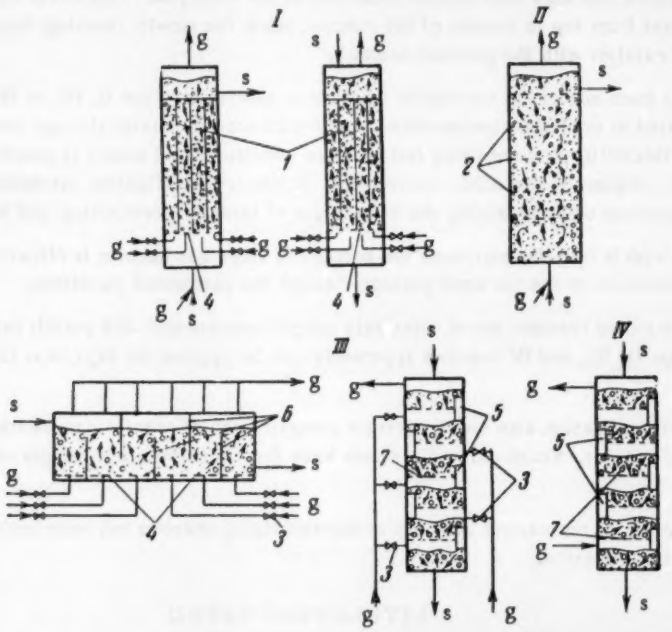


Fig. 7. Basic designs for sectionalization of flow-type reactors with internal mixing for heterogeneous systems: I) Parallel sectionalization; II) series sectionalization; III) stepwise introduction of gaseous component, in combination with series sectionalization for solid component; IV) stepwise countercurrent; g) gaseous component; s) solid powdered component (catalyst); 1) parallel elements; 2) perforated partitions, grating; 3) manifold valves for regulating gas feed; 4) gas distribution apparatus (calibrated master tap, nozzles, grates, etc.); 5) overflow device for pseudoliquid [fluidized powder]; 6) dead-end partitions; 7) cap plates, perforated partitions, or grates.

The basic possibilities are the following types of reactors with both solid and gas flow: ideal [complete] mixing; parallel sectionalization; series or stepwise sectionalization; stepwise introduction of reactants; stepwise countercurrent.

The flow plans of sectionalized reactors are shown in Fig. 7 [1, 10].

In parallel-sectionalized reactors (Type I) the solid dividing partitions serve mainly for suppressing longitudinal and transverse currents. As a result, the intensity of mixing of raw material and conversion products is decreased, which makes it easier to obtain a deep degree of conversion upon passing through the reactor, even in the case of reversible and complex reactions. However, decreasing the intensity of intrareactor mixing makes it difficult to regulate the temperature conditions in rapid temperature-sensitive reactions with pronounced heating effects and highly irregular rate. For high flexibility of control of temperature conditions in such reactors it is necessary to intensify by all possible means the heat exchange across the dividing surfaces of the sections.

With series sectionalization (Type II), mixing of the reacting streams takes place only at the boundaries of each of the successive sections, with a low concentration gradient. Therefore the influence of intrareactor circulation on the process is reduced, and the intensive mixing within each of the sections creates temperature uniformity within it.

In the Group III reactors the principle of series sectionalization is combined with multistage introduction of the most reactive reactant. By these means the rate and the heat removal are equalized along the length of the contacting apparatus, which ensures uniform and intensive course of the process along with high selectivity.

Reactors with Type IV sectionalization combine the principle of successive deepening of the process with counterflow of the heterogeneous system (catalyst and reactants). Counterflow makes it possible to attain very great conversion depths and high equilibrium activities of the catalysts. This evens out the reaction rates and the rates of heat removal from top to bottom of the reactor, since the slowly reacting deeply converted stream is contacted by fresh catalyst with the greatest activity.

Upon transfer from one of the successive sections to another in Type II, III, or IV reactors, the reacting stream may be heated or cooled by intrasectional heat-exchange apparatus through the surface or by mixing. All of this ensures flexibility in controlling temperature conditions and makes it possible to come near to the optimum, even for complex or reversible conversions. Series sectionalization minimizes the harmful effect of mixing on these processes while retaining the advantages of intensive contacting and heat exchange of the phases.

In apparatus with horizontal partitions the passage of large gas bubbles is effectively eliminated, owing to repeated cross-distribution of the gas upon passage through the perforated partitions.

Series-sectionalized reactors are of relatively simple construction and permit saving of metal as compared to other types. Type II, III, and IV reactors apparently can be applied for high heat loads and large raw-material capacity.

Although sectionalization also entails certain complication of reactor construction, it reduces the specific cost of metal in the reactor. Sectionalized reactors have the undeniable advantages of more intensive and uniform reaction.

The effectiveness of the various methods of sectionalizing reactors has been verified by many studies and by many years of plant practice.

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SIMON ZALMANOVICH ROGINSKII (on his 60th Birthday)

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On March 25, 1960, the outstanding physical chemist Simon Zalmanovich Roginskii, Corresponding Member of the Academy of Sciences of the Soviet Union, celebrated his 60th birthday.

The major portion of the researches carried out by S. Z. Roginskii, or under his direction, has had to do with problems of kinetics and catalysis.

As early as his twenties, while studying the catalytic decomposition of oxygen-containing compounds such as potassium chlorate and potassium permanganate, S. Z. Roginskii directed attention to the fact that colored substances capable of electronic conductivity showed the greatest catalytic activity. It was considerably later that the connection between the color of the catalyst and its catalytic activity was also recognized for the catalytic oxidation of organic compounds. In 1935 the phenomenon of gaseous promoting of metallic catalysts was revealed. Further work, carried out under the direction of S. Z. Roginskii, revealed the existence of a link between the catalytic activity of solid materials and other electronic properties, such as the conductivity, electronic work function and others, together with the effect of microimpurities on the formation of an active surface. The result of these discoveries was the development of an electron-chemical approach to catalysis. In the subsequent years catalysis on solid semiconductors was studied very fruitfully in S. Z. Roginskii's laboratory.

According to the views developed by S. Z. Roginskii, all the varied catalytic processes may be divided into two principal classes: oxidation-reduction processes (electronic) and acid-base (ionic). For processes of the first kind, the catalysts are electron donors or electron acceptors, such as metals and semiconductors; for processes of the second kind, the catalysts are proton donors or proton acceptors, such as solid acids and bases. The mechanism of processes in both classes has been studied in detail under S. Z. Roginskii's direction.

S. Z. Roginskii is the author of one of the first theories of the preparation of catalysts, the supersaturation theory. According to this theory, the most active catalysts are obtained when the preparation process leads to a nonequilibrium condition. The theory has made it possible to effect improvements in certain technical catalysts.

S. Z. Roginskii and his collaborators have shown that the surface of most catalysts is nonhomogeneous, and have formulated a statistical theory of processes occurring on nonhomogeneous surfaces. By means of this theory it is possible to explain a number of regularities which are observed in the kinetics of catalytic reactions and of chemisorption. The results of this group of investigations has been published in the monograph "Adsorbtsiya i

kataliz na neodnorodnykh poverkhnostyakh" (Adsorption and Catalysis on Nonhomogeneous Surfaces, (1948).

In S. Z. Roginskii's laboratory investigations have been carried out on the mechanism of the catalysts for a number of important industrial reactions: the oxidation of hydrocarbons, cracking, the hydrogenation of fats, the synthesis of divinyl from alcohol, the synthesis of hydrocarbons from carbon dioxide and hydrogen, and others.

S. Z. Roginskii has also always been interested in problems of catalysis in the solid state. Towards the end of the twenties he conducted a study of the decomposition of explosive materials. Subsequently (together with O. M. Todes) he formulated a crystallization theory of topochemical (localized) reactions.

S. Z. Roginskii paid great attention to the developing of new methods of investigation in kinetics and catalysis. In 1935 he was the first in the Soviet Union (together with N.E. Brezhneva) to apply artificial radioisotopes for the study of the mechanism of chemical reactions. In 1956 his fundamental monograph, "Teoreticheskie osnovy izotopnykh metodov izucheniya khimicheskikh reaktsii" (Theoretical Bases of Isotopic Methods of Studying Chemical Reactions), was issued. His investigations (in collaboration with A. B. Shekhter and I. I. Tret'yakov) in the field of electron microscopy of catalysts and disperse materials are widely known. Recently his laboratory has witnessed the successful development of chromatographic and radiochromatographic methods of analysis, the emission projector method, various methods of measuring the electrical properties of catalysts, etc.

S. Z. Roginskii is the author of more than three hundred scientific works in the fields of kinetics, catalysis and other departments of physical chemistry. Many of his works have been translated into other languages.

S. Z. Roginskii commenced his scientific activity under the direction of Academician D. P. Konovalov and Academician L. V. Pisarzhevskii in Dnepropetrovsk, and afterwards worked in the institutes in Leningrad under the direction of Academician A. F. Ioffe and Academician N. N. Semenov. From 1932 he became the permanent director of the Laboratory of Catalysis in the Institute of Chemical Physics, and from 1942 he occupied the same position in the Institute of Physical Chemistry of the Academy of Sciences of the Soviet Union. In 1939 he was elected to be a Correspondent Member of the Academy of Sciences of the Soviet Union. S. Z. Roginskii gave much attention to the training of scientific recruits, and he was the director of departments in the Leningrad Polytechnic Institute and the Moscow Institute of Chemical Machine-Construction.

More than forty candidate dissertations were issued under the direction of S. Z. Roginskii. About twenty Doctors of Science began their studies in his laboratory, among them such eminent Scientists as Academician Ya. B. Zel'dovich, Correspondent Member of the Academy of Sciences of the Soviet Union L. M. Sapozhnikov, and Doctors of Science O. I. Leipunskii, O. M. Todes, N. E. Brezhneva, S. Yu. Elovich and others.

The Editorial Office of "Kinetika i Kataliz", together with all soviet scientists working in the field of catalysis, congratulate Roginskii on this anniversary, and wish him many years of life and fruitful scientific activity.

CURRENT EVENTS

ALL-UNION CONFERENCE ON ORGANIC CATALYSIS IN MOSCOW

E. I. Klabunovskii

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Original article submitted December 15, 1959

The first All-Union conference on organic catalysis was held in Moscow from November 16 to November 20. It was organized on the initiative of the Scientific Council on the problem: "Scientific Principles of Catalysts Selection" by the Institute of Organic Chemistry of the Academy of Sciences USSR, the L. Ya. Karpov Physicochemical Institute, and the Chemical Faculty of the Moscow State University.

In view of the fact that the State Committee for Chemistry of the Council of Ministers USSR intended to hold a conference on technical catalysis at the same time, it was decided to combine the two conferences. Some 600 representatives from scientific institutes of the Academy of Sciences USSR and academies of sciences of the Union republics, higher educational establishments, and industrial institutes took part in the work of the conference; more than 30 cities of the Soviet Union were represented.

About 160 papers and scientific communications were presented at the conference; the summaries were preprinted in the conference program.

Eight papers on theoretical aspects of organic catalysis, concerned mainly with structure and energy relationships in catalysis and electronic concepts in semiconductor catalysis, were presented at the plenary sessions. Ten papers of the survey type were presented on aspects of technical catalysis.

The remaining papers and reports on experimental work were distributed between six sections: 1) Investigations of catalysts; 2) Polymerization and condensation reactions; 3) Isomerization and alkylation reactions; 4) Hydrogenation, dehydrogenation, and dehydrocyclization reactions; 5) Hydration, dehydration, and hydrolysis reactions; 6) Oxidation and halogenation reactions.

In his introductory address at the opening of the conference Academician B. A. Kazanskii referred to the scope of the research on organic catalysis being conducted in various institutions all over the Soviet Union, and expressed his confidence that the subject matter of these investigations would be reflected in the work of the conference.

In a paper entitled "Molecular structure and reactivity" Academician A. A. Balandin (IOKh AN SSSR)* examined applications of modern theories of the structure of matter to organic noncatalytic, homogeneous-catalytic, and heterogeneous-catalytic reactions. Whereas in the case of organic noncatalytic reactions the relationship between reactivity and molecular structure has been largely worked out in the light of electron concepts, and some qualitative assessments are possible in homogeneous catalysis, in heterogeneous catalysis clarification of this relationship is complicated by the presence of solid catalysts, although the elementary stages of the process turn out to be simpler. Existing data and new results on hydrogenation and dehydrogenation of hydrocarbons and on dehydrogenation and dehydration of alcohols were presented in the paper. The influence of induction effect and conjugation energy in side-chain substituents on the bond lengths and energies in the principal chain, which influence the reaction rate, was considered.

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The paper by S. Z. Roginskii (IFKh AN SSSR)* detailed the basic principles of the generalized theory of catalysis, which takes into account electronic effects, influence of surface coverage on activation energy, composition of the adsorption layer, and surface heterogeneity. Electron transitions between the catalyst and the reacting molecule are probable in the reaction. Changes of the work exit function are decisive in variations of catalyst activity and selectivity as the results of modification. The main forms of modification associated with changes of the work exit function and the probable origin of compensation effects in catalysis were considered.

The paper by F. F. Vol'kenshtein (IFKh AN SSSR) was also concerned with electronic factors in the kinetics of heterogeneous reactions.

The relative contents of forms in different stages of chemisorption on a semiconductor surface depend on the position of the Fermi level. The activity of a catalyst may be varied within certain limits by displacement of that level. Two opposing effects (promotion and poisoning) of the same impurity on two types of reactions, which are accelerated when the Fermi level is raised or lowered, were considered in the paper. Applications of the general principles of the electronic theory of catalysis were illustrated by examples of oxidation of CO and dehydration and dehydrogenation of alcohols.

In a paper on the use of infrared spectra of adsorbed molecules for investigation of oxide and metallic catalyst surfaces A. N. Terenin (jointly with L. M. Roev, Leningrad State University) showed that adsorption of NO on oxides of Ni, Cr, Fe, Si, Zn, and Al can occur both on oxygen ions and on metal ions (in the case of transition elements). Additions of some oxides to others alter considerably the acceptor behavior of metal ions.

N. P. Keier (IFKh AN SSSR) reported on the influence of electronic interaction of molecules through solids on the activation energy of chemisorption of acetylene on nickel. This mutual influence, studied by the isotope desorption method, is detected at very low degrees of surface coverage. However, surface heterogeneity has a considerably stronger influence than electronic interaction of molecules adsorbed on a solid surface on changes of the activation energy of adsorption with degree of surface coverage.

S. L. Kiperman (jointly with I. R. Davydova, IOKh AN SSSR) reported on various methods for quantitative assessment of bonding energies between surface compounds and metallic catalysts (Ni, Pd). The values found for the energies of bonding between C, H, and N and the catalyst were used for calculation of the activation energies for hydrogenolysis of methylamine and five-membered rings.

The American scientist Prof. R. L. Burwell, Jr. (Chemistry Department, Northwestern University, Evanston, Ill. USA), who took part in the work of the conference, reported on reactions between hydrocarbons and deuterium in presence of chromium oxide. He considered the mechanisms of isotope exchange reactions between deuterium and alkanes and cycloalkanes, isotopic distribution of deuterium–olefin addition products, stereochemistry of addition to cis- and trans-butene-2 and to 1,2-dimethylcyclohexene, and exchange with (+)-3-methylcyclohexane. Cyclopropane exchanges hydrogen much more rapidly than other hydrocarbons. In contrast to the reaction on metallic catalysts, addition of D_2 to ethylene on chromium oxide at −78° gives pure 1,2-di-D-ethane. Rise of temperature favors formation of multiple-exchange products.

E. I. Klabunovskii (IOKh AN SSSR) described the application of stereospecific catalysis to determinations of the absolute configurations of molecules. In catalysis there is a correspondence between the configuration of the molecule of butanol-2 and the structure of optically active quartz (support for a number of catalysts); it follows from this that (+)-butanol-2 has an absolute configuration belonging to the L series.

In the discussion, M. A. Landau, in his own name and on behalf of V. V. Shchekin (INKhS AN SSSR), reported on certain aspects of catalytic activity of oxide and metallic catalysts.

About 140 papers were presented at the sections.

The section of catalyst investigation discussed new methods for studying catalysts: application of methods of electron paramagnetic resonance to studies of chromium catalysts (V. V. Voevodskii, V. B. Kazanskii, and Yu. I. Pecherskaya, IFKh AN SSSR), radiochemical and radiochromatographic techniques and studies of the electronic exit work function (S. Z. Roginskii, M. I. Yanovskii, É. Kh. Enikeev, and L. Ya. Margolis, IFKh AN SSSR), studies of reaction kinetics and phase composition of alloy catalysts (D. I. Lainer and N. M. Kagan, State Institute for

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Planning of Nonferrous Metal Processing Plants, and V. V. Patrikeev, IOKh AN SSSR), measurements of electrical conductivity of sprayed metal films (V. M. Gryaznov, MGU), measurements of contact potential differences for catalysts (M. T. Rusov and V. M. Vlasenko, Institute of Physical Chemistry, Academy of Sciences UkrSSR), and studies of the magnetic properties of catalysts (A. A. Slinkin, IOKh AN SSSR).

Several investigations were concerned with the effects of additives on activity of nickel catalysts (G. D. Lyubarskii, L. N. Ivanovskaya, and G. G. Isaeva, L. Ya. Karpov Physicochemical Institute) and of semiconductor catalysts (G. M. Zhabrova, V. I. Vladimirova, and O. M. Vinogradova, IFKH AN SSSR).

The effects of pore size and specific surface of the support and catalyst (A. M. Rubinshtein, IOKh AN SSSR; É. M. Kaganova, T. E. Shakhova, and A. E. Panitkova, All-Union Scientific Research Institute of Petrochemicals) on catalyst activity were studied; radiosulfur was used for studying the influence of poisoning of metallic catalysts by sulfur compounds (Kh. M. Minachev, G. V. Isagulyants, and D. A. Kondrat'ev, IOKh AN SSSR).

The influence of gas treatment (with atomic hydrogen, etc.) on activity and selectivity of chromium oxide was investigated (I. D. Rozhdestvenskaya, IOKh AN SSSR). Several new observations concerning the nature of active centers were made: formation of two types of surface compounds in bifunctional catalysts (T. V. Antipina, MGU), the possible existence of parallel as well as perpendicular orientation of alcohol molecules in monolayers in adsorption of Al_2O_3 (M. P. Maksimova and V. É. Vasserberg, IOKh AN SSSR), which is of great interest in relation to enzyme action. It was established by the differential isotopic method that there are two types of centers on Al_2O_3, which catalyze exchange or dehydration (O. V. Krylov and E. A. Fokina, IFKh AN SSSR).

Subjects considered in the section dealing with polymerization and condensation reactions included stereo-directed polymerization of α-olefins (B. A. Krentsel', A. V. Topchiev, INKhS AN SSSR) and polymerization of propylene on alumina–silica and silica–tungsten oxide catalysts (Ch. S. Karryev, G. M. Panchenkov, and S. V. Al'tshuler, I. M. Gubkin Petrochemical and Gas Industry Institute, E. G. Vol'pova and L. I. Ogloblina, Groznyi, Scientific Research Institute). Considerable attention was devoted to discussion of the mechanism of catalysis (Ya. T. Éidus, IOKh AN SSSR) and investigations of catalysts for synthesis based on CO and H_2 (A. N. Bashkirov, Yu. B. Kagan, Yu. B. Kryukov, and S. M. Loktev, Institute of Petrochemical Synthesis, AN SSSR).

Several new examples of condensation were reported: production of higher alcohols from lower in presence of $Cu-TiO_2$ catalyst (B. A. Bolotov and P. M. Adrov, Leningrad State University), and synthesis of thiophene by condensation of SO_2 with butene-2 (A. V. Topchiev, G. M. Tsiguro, and G. I. Dmitrieva, I. M. Gubkin Petrochemical and Gas Industry Institute).

The alkylation and isomerization section was concerned with the mechanism of paraffin isomerization in presence of Pt or Pd catalysts supported on Al_2O_3 or aluminosilicates (N. G. Bekauri, N. I. Shuikin, T. S. Shakarashvili, Institute of Chemistry, Academy of Sciences Georgian SSR; G. N. Maslyanskii, N. R. Bursian, and S. A. Barkhan, All-Union Scientific Research Institute of Petrochemicals), or nickel catalysts on kieselguhr (M. I. Ryskin and M. S. Nemtsov, All-Union Scientific Research Institute of Petrochemicals). Isomerization of cyclohexane to methylcyclopentane under pressure (M. G. Gonikberg, I. I. Levitskii, and B. A. Kazanskii, IOKh AN SSSR) and of bicyclanes to decahydronaphthalenes (M. B. Turova-Polyak and I. E. Sosnina, MGU) was studied. A new reaction of isomerization of a number of furan compounds into aliphatic alcohols and aldehydes in presence of Pt was investigated (N. I. Shuikin and I. F. Bel'skii, IOKh AN SSSR).

Several communications were concerned with alkylation of benzene over aluminosilicate catalysts (G. M. Panchenkov and I. M. Kolesnikov, I. M. Gubkin Petrochemical and Gas Industry Institute; N. V. Rudenko and M. B. Turova-Polyak, MGU) and with the aid of aluminum chloride (R. M. Lagidze, Institute of Chemistry, Academy of Sciences, Georgian SSR). Allylation of phenols and phenolic ethers in presence of copper catalysts was studied (S. G. Mel'kanovitskaya and I. P. Tsukervanik, Institute of Chemistry, Academy of Sciences Uzbek SSR).

Most of the papers were concerned with researches on hydrogenation, dehydrogenation, and dehydrocyclization.

In the hydrogenation field, the section discussed mechanism and kinetics of hydrogenation of ethylene over Pd (L. O. Apel'baum and M. I. Temkin, L. Ya. Karpov Physicochemical Institute) and Ni/Al_2O_3 (A. Ya. Rozovskii, V. V. Shchekin, and E. G. Pokrovskaya, Institute of Petrochemical Synthesis, Academy of Sciences USSR), and kinetics of benzene hydrogenation over an industrial catalyst (L. M. Kachkina, G. K. Boreskov, and G. D. Lyubarskii, L. Ya. Karpov Physicochemical Institute.

D. V. Sokol'skii and his associates (Institute of Chemistry, Academy of Sciences Kazakh SSR) presented a number of communications on liquid-phase hydrogenation kinetics; these included the report of a study of the influence of the nature of the solvent or strongly adsorbed component on the hydrogenation rates of unsaturated and nitro compounds (terephthalic acid dinitrile, etc.)in presence of Pt, Pd, and Ni. The synthesis and conversion of furanamines (A. N. Ponomarev, N. P. Maslennikova, and N. V. Alakina, Saratov State University) and hydrolytic hydrogenation of wood (N. A. Vasyunina, A. A. Balandin, and S. V. Chepigo, IOKh AN SSSR and All-Union Scientific Research Institute of the Hydrolysis and Sulfite Alcohol Industry) were studied.

Several papers dealt with conditions for dehydrogenation of C_4 and C_5 hydrocarbons (Chang Chao-lan K. P. Lavrovskii, and A. L. Rozental', Institute of Petrochemical Synthesis, Academy of Sciences USSR; D. A. Bol'shakov and I. Ya. Tyuraev, NIIM SK; I. L. Fridshtein, State Institute for the Planning of Rubber Industry Plants; V. S. Aliev, A. P. Kasimova, Sh. K. Kyazimov, and Ter-Sarkisov, Institute of Petrochemical Industry, Academy of Sciences Azerbaidzhan SSR). Studies of new dehydrogenation catalysts for six-membered rings and alcohols were reported: rhenium on supports (E. I. Karpeiskaya and A. A. Tolstopyatova, M. A. Rumyantseva and Kh. M. Minachev) and cadmium oxide (V. A. Ferapontov, IOKh AN SSSR). The use of zinc in selective hydrogenation of unsaturated aldehydes and other compounds was also described.

Six papers were concerned with dehydrocyclization studies. Cyclopentanes and aromatic hydrocarbons were prepared from paraffins in presence of Pt/carbon catalyst (B. A. Kazanskii, A. L. Liberman, M. I. Rozengart, A. Z. Dorogochinskii, A. V. Lyuter, and M. G. Mitrofanov, IOKh AN SSSR and Groznyi Scientific Research Institute). Dehydrogenation was also studied in presence of gumbrin and molybdenum oxide – alumina catalyst with added SrO (Kh. I. Areshidze, Institute of Chemistry, Academy of Sciences, Georgian SSR; M. S. Belen'kii and Ya. P. Skorupko, Azerbaidzhan Institute of Petroleum Chemistry). An effective catalyst, containing TiO_2, has been developed for cyclization of o-nitroethylbenzene into indole (K. A. Krupennikova, Kazakh State University).

Eighteen papers were presented at the section dealing with hydration, dehydration, and hydrolysis.

A stable Si–B–W catalyst for direct hydration of ethylene has been developed (E. M. Piskunova, G. K. Boreskov, and V. A. Dzis'ko, L. Ya. Karpov Physicochemical Institute), and equilibrium and kinetics of ethylene hydration were studied (Yu. M. Bakshi, A. I. Gel'bshtein, and M. I. Temkin, L. Ya. Karpov Physicochemical Institute).

A report was made on work in progress on partial replacement of the mercury catalyst for acetylene hydration, and on searches for certain general principles of catalyst selection for acetylene-addition reactions, including hydrochlorination of acetylene (R. M. Flid, Moscow Institute of Fine Chemical Technology).

Several communications dealt with the use of ion-exchange resins as catalysts in various reactions, as in certain cases they are more effective than acid catalysts (V. I. Isagulyants, I. M. Gubkin Petrochemical and Gas Industry Institute; N. S. Rabovskaya, G. A. Razuvaev, T. I. Andrianova, and B. P. Bruns, IFKh AN SSSR).

Energies of bonding between C, H, O and catalysts were determined by means of model reactions of dehydration (and dehydrogenation) of alcohols in presence of WO_3 and BeO catalysts (V. Stshizhevskii and A. A. Tolstopyatova, MGU; M. Ya. Yakushina, MIIGS).

In the section on oxidation and halogenation 20 papers were presented.

Studies of the oxidation of propylene to acrolein occupied a prominent place. Stable and selective catalysts based on group VI and VII elements have been developed, and the optimum reaction conditions have been determined (Yu. D. Kernos and B. L. Moldavskii, All-Union Petrochemical Scientific Research Institute). Copper catalysts (the $Cu_2O + Cu + CuO$ system) for oxidation were also studied (N. I. Popova, E. E. Vermel', V. N. Latyshev, and F. A. Mil'man, IKh VSF AN SSSR; L. Ya. Margolis, M. Ya. Rubanik, and A. V. Gershingorin, Institute of Physical Chemistry, Academy of Sciences Ukrainian SSR).

New catalysts for oxidation of butylene and butane have been developed, and the optimum conditions for oxidation of furfural to maleic anhydride were determined (B. L. Moldavskii and Yu. D. Kernos, All-Union Petrochemical Scientific Research Institute; V. A. Slavinskaya, S. A. Giller, and I. I. Ioffe, Institute of Organic Chemistry, Academy of Sciences, Latvian SSR).

A silver catalyst for oxidation of ethylene to ethylene oxide was investigated, and the effects of additives were studied (M. I. Temkin and N. V. Kul'kova, L. Ya. Karpov Physicochemical Institute; L. Ya. Margolis, É. Kh. Enikeev, O. V. Isaev, and V. R. Linde, IFKh AN SSSR).

The macrokinetics of naphthalene, naphthoquinone, and phthalic anhydride oxidation over a vanadium catalyst was studied (G. P. Korneichuk, V. A. Roiter, and V. P. Ushakova, Institute of Physical Chemistry, Academy of Sciences, Ukrainian SSR). The kinetics of oxidation of ethylene glycol to glyoxal was investigated (N. V. Klimova, A. I. Tishchenko, and I. I. Ioffe, NIOPiK.

Problems of technical catalysis were discussed at the final plenary session. The paper by K. G. Boreskov and V. S. Chesalova (L. Ya. Karpov Physicochemical Institute) dealt with production of catalysts on the industrial scale. The principal characteristics required in industrial catalysts were specified, and methods were described for regulation of the internal surface area, pore structure, grain shape and size, and other characteristics which determine catalyst properties. The paper concluded with recommendations for improving the production of industrial catalysts.

V. A. Roiter (Institute of Physical Chemistry, Academy of Sciences, Ukrainian SSR) discussed the defects of existing methods for measurement of catalytic activity and suggested that methods of catalyst testing should be standardized.

M. G. Slin'ko (Institute of CO Catalysis, Academy of Sciences USSR) discussed methods for scale modeling and calculation of catalytic reactors. He showed that in a number of cases the laws of catalysis and modeling principles can be used, with the aid of electronic computers, for passing directly from the results of laboratory experiments to industrial equipment, or for reducing the number of intermediate experimental plants.

Other papers dealt with modeling of isothermal reactors with fixed, suspended, or fluidized catalyst beds, and with methods of calculation for processes controlled by diffusion (V. B. Fal'kovskii, Moscow Institute of Fine Chemical Technology, I. I. Ioffe, NIOPiK; O. M. Todes, VITU VMF). M. E. Aerov (NIISS), showed that longitudinal thermal conductivity and diffusion are of great importance in catalyst testing. Automation of catalytic processes has received considerable attention (N. N. Shumilovskii, Moscow Power Institute).

The conference was marked by a high degree of activity of its participants. Most of the papers provoked likely discussions. Between 40 and 200 persons attended the sectional meetings.

Large teams of workers in the catalysis field, recently formed in the Academies of Sciences of the Ukrainian, Kazakh, Belorussian, and Uzbek SSR, took part in the conference. About one half of the papers were presented by provincial delegates. Many of the papers were by young scientists.

Several organizational measures for intensifying work on organic and technical catalysis were recommended at the conference.

The conference approved the work of the Scientific Council on the problem: "Scientific Principles of Catalyst Selection" and expressed the desire that work on technical catalysis should be expanded to the utmost. The need for a reference index containing data on the applicability ranges and properties of the most important catalysts produced in our factories was noted.

The conference recommended that All-Union conferences should be held in the immediate future on methods of testing industrial catalysts, homogeneous catalysis, and oxidation catalysis. The conference noted with satisfaction the organization of the Institute of Catalysis of the Siberian Division of the Academy of Sciences in Novosibirsk, and the publication of the new journal "Kinetics and Catalysis."

The conference demonstrated the growing role of organic catalysis in solution of many problems of practical importance. Applications of structural energy and electronic concepts of elucidation of several problems in the theory of catalysis were shown to be fruitful, and the convergence of different viewpoints on catalytic phenomena, noted previously, was confirmed.